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BUREAU OF STANDARDS JOURNAL OF RESEARCH

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THE LIFE OF THE SAGGER AS AFFECTED BY VARYING CERTAIN PROPERTIES

By R. A. Heindl and L. E. Mong

ABSTRACT

This report presents the results obtained in a study of sagger bodies and represents an enlargement of a similar study of a preliminary nature, the results of which have been published. The clays and grogs are combined to give bodies having wide variations in body structure and in the several properties which were studied. Data are given on the modulus of elasticity, transverse breaking strength, plastic flow, thermal expansion, and resistance to failure due to heat shock of 35 laboratory-prepared bodies and 10 commercial bodies after firing at from 1 to 3 different temperatures. For comparative purposes data are given on two series of bodies—the one series containing coarse grog and the other fine grog. In addition, body compositions were varied in order to compare the effect on sagger life of using open and close burning grogs.

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I. INTRODUCTION

The investigation of the properties of sagger clays and sagger bodies has been in progress at the Bureau of Standards for a number of years, and as the study has progressed reports[1] have been issued covering the completed phases. Since the results given in the preceding report were of a preliminary nature, it was considered advisable to continue the study of sagger bodies with special reference to the effect of porosity, thermal expansion, and moduli of rupture and elasticity on the resistance of saggers to failure due to thermal shock. This paper contains the results of tests made on 35 different laboratory-prepared sagger bodies as well as on 10 sagger bodies furnished by industrial potteries, all of which were fired at from one to three different temperatures.

[1] Progress Report on Investigation of Sagger Clays, J. Am. Ceram. Soc., vol. 9 (3), pp. 131-143; 1926. II. Progress Report on Investigation of Sagger Clays—Some Observations as to the Significance of Their Thermal Expansion, J. Am. Ceram. Soc., vol. 9 (9), pp. 554-574; 1926. III. Progress Report on Investigation of Sagger Clays—Their Elasticity and Transverse Strength at Several Temperatures, J. Am. Ceram. Soc., vol. 10 (7), pp. 524-534; 1927. IV. Progress Report on Investigation of Sagger Clays—Their Elasticity, Transverse Strength, and Plastic Flow at 1,000° C., J. Am. Ceram. Soc., vol. 10 (12), pp. 995-1004; 1927. Preparation of Experimental Sagger Bodies According to Fundamental Properties, B. S. Jour. Research, vol. 3 (RP104); also J. Am. Ceram. Soc., vol. 12 (7), pp. 457-480; 1929.

II. SAGGER BODY COMPOSITIONS

All of the bodies contained equals parts by weight of bond clay and grog, but variations in the bond clay and grog were introduced by using different combinations of clays and of grogs in several of the mixes. The grogs used were fired at approximately 1,230° C. (cones 9 to 9½) for one and one-half hours. The sagger body numbers, the laboratory numbers of the clays used as bond and as grog and the percentages of each used in making up the various bodies are given in Table 1.

TABLE 1.—*Sagger body numbers, and composition of bodies and porosity of fired clay*

(Table does not include bodies furnished by potteries)

Sagger body No.[1]	Laboratory No. of bond clays	Percentage of each clay used	Laboratory No. of grog clays	Percentage of each grog used
1BF, 1BC [2]	21, 47	50	15, 42	50
2BC	21, 47	50	19, 24	50
3BF	21, 50	50	19, 24	50
4BF, 4BC	10, 40	50	5, 41	50
5BF, 5BC	26	75	26, 51	50
	51	25		
6BF, 6BC	19, 26, 51	33⅓	26, 51	50
7BF, 7BC	22	40	28, 36	50
	46	60		
8BF, 8BC	11	25	9, 43	50
	28	25		
	50	50		
9BF, 9BC	43, 44	50	43, 44	50
10BF, 10BC	8, 45	50	8, 45	50
11BF, 11BC	8, 45	50	45	100
12BF, 12BC	8, 45	50	8	100
13BF, 13BC	22	40	1, 12	50
	29	60		
14BF, 14BC	39, 44, 45	33⅓	2, 4	50
15BF, 15BC	21, 46	50	21, 46	50
16BF, 16BC	21, 46	50	21	100
17BF, 17BC	21, 46	50	46	100
18BC	(3)	100	22, 39	50
19BC	(3)	100	22	100
20BC	(3)	100	39	100

[1] Bodies containing the fine grog are designated F, those containing the coarse grog, C. The letter B is used with the body number to differentiate these bodies from those in the preceding reports.

[2] Bodies 1BF to 4BC, inclusive, contained grog prepared from saggers used for tests referred to in the preceding report (see footnote 6) and may be identified by the numbers of the grog clays. The remaining bodies contained grog prepared from clays independently fired and afterwards mixed in the proper proportions.

[3] Commercial mix.

The majority of the bodies were prepared, as in previous work, in two series. One series compounded with comparatively coarse sizes of graded grog was designated as C and the other series compounded with the finer sizes of graded grog was designated as F.

The grog sizing and the percentages of each size were as follows:

Material	Passed through sieve No. —[1]	Retained on sieve No. —[1]	Percentage of each size
For coarse grogged body	4	8	20
	8	12	60
	12	20	20
For fine grogged body	20	40	66⅔
	40	80	33⅓

[1] United States standard series.

Five bodies were prepared using dense and open burning grogs and a commercially prepared mixture of sagger clays.

III. DESCRIPTION OF SPECIMENS

The specimens were prepared and tested in a manner similar to that described in the Fifth Progress Report.[2] In order to obtain a gradational change in the porosity and other physical properties, a large proportion of the saggers and specimen bodies were fired at three different temperatures, namely, approximately 1,190° C. (cones 7½ to 8); 1,230° C. (cones 9½ to 10); 1,270° C. (cones 11 to 12).

IV. METHODS OF TESTING

The methods of determining the modulus of rupture, porosity, resistance to thermal shock, linear thermal expansion, modulus of elasticity, and plastic flow have been described in detail in the several previous progress reports.[3]

V. RESULTS

The complete results obtained are summarized in Table 2. The body numbers are followed directly by the number of the pyrometric cone to which the particular saggers and specimen bars were fired.

1. MODULUS OF RUPTURE AND SHRINKAGE, UNFIRED BODIES

The average modulus of rupture for the laboratory-prepared bodies which contained the fine grog was 155 lbs./in.^{2}, for bodies which contained the coarse grog 115 lbs./in.^{2}, and for commercial bodies 80 lbs./in.^{2}

The average linear drying shrinkage for the fine-grogged bodies was 4.2 per cent, the coarse-grogged bodies 3.0 per cent, and the commercial bodies 3.4 per cent.

2. PROPERTIES OF THE BODIES AFTER FIRING

The porosities of the bar specimens as well as those of the saggers are given in Table 2. Each of the values represents the average of not less than three determinations.

The total linear thermal expansion for the ranges from atmospheric temperature to 250° C. and from atmospheric temperature to 1,000° C., as well as the coefficient for the former range are given. The determinations were made on specimens prepared from the ruptured bars used for the strength and elasticity tests. Duplicate determinations were made on all specimens.

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[2] See last reference of footnote 1, p. 1017.

[3] See footnote 1, p. 1017.

TABLE 2.—*Properties of sagger bodies*

Body No. and cone at which fired	Modulus of rupture of unfired body	Dry shrinkage	Fired shrinkage	Tested at 20° C.			Tested at temperature at which sagger failed in quenching test				Tested at 1,000° C.		Total plastic deflection in inches (taken from plastic flow curves). Stress of approximately—		Porosity of bars	Porosity of saggers	Total expansion from atmospheric temperature to 250° C.	Coefficient of expansion atmospheric temperature to 250° C.	Total expansion from atmospheric temperature to 1,000° C
				Modulus of—		Computed[1] outer fiber strain	Modulus of—		Computed[1] outer fiber strain	Sagger[2] failing at	Modulus of—								
				Rupture	Elasticity		Rupture	Elasticity			Rupture	Elasticity	120 lbs./in.[2]	240 lbs./in.[2]					
	Lbs./in.[2]	*Per cent*	*Per cent*	*Lbs./in.*[2]	*1,000 lbs./in.*[2]	*Per cent*	*Lbs./in.*[2]	*1,000 lbs./in.*[2]	*Per cent*	*°C.*	*Lbs./in.*[2]	*1,000 lbs./in.*[2]	$\times 10^{-4}$	$\times 10^{-4}$	*Per cent*	*Per cent*	*Per cent*	$\times 10^{-6}$	*Per cent*
1BF-8+	180	4.3	1.5	1,720	3,370	0.051	1,785	4,050	0.044	565	2,260	450	9	33	27.2	26.6	0.12	5.4	0.52
1BF-10+	180	4.3	2.1	1,725	3,800	.045	1,570	3,720	.042	540	1,910	455	12	33	24.0	21.7	.11	5.1	.50
1BF-12	180	4.3	2.4	2,095	5,380	.039	1,960	5,440	.036	525	2,710	555	9	21	20.0	19.2	.11	4.7	.47
1BC-8+	130	3.5	1.0	955	2,100	.045				635	1,010	295	14	52	27.2	26.3	.13	5.7	.53
1BC-10+	130	3.5	1.4	995	2,305	.043	900	3,140	.029	610	1,255	325	14	50	25.0	21.6	.11	5.0	.49
1BC-12	130	3.5	2.7	1,130	3,095	.036	1,250	3,670	.034	585	1,650	365	85	35	21.0	21.9	.11	4.8	.50
2BC-8+	105	2.7	1.7	480	715	.067	860	1,335	.064	865	780	300	12	49	37.0	37.8	.14	6.3	.55
2BC-10+	105	2.7	2.2	470	755	.062	725	1,235	.059	860	825	305	10	47	35.3	31.2	.13	5.7	.52
2BC-11+	105	2.7	2.6	495	930	.053	695	1,515	.046	775	900	320	6	42	32.4	32.0	.13	5.7	.49
3BF-8+	130	4.5	.9	695	990	.070	1,115	2,165	.051	690	1,055	475	7	25	36.4	35.8	.13	5.8	.53
3BF-10+	130	4.5	1.3	815	1,140	.071	870	2,190	.040	635	1,340	545	5	15	34.4	32.3	.15	6.4	.54
3BF-11+	130	4.5	1.8	1,095	1,565	.070	1,200	2,300	.052	610	1,630	695	4	13	32.8	32.4	.16	7.0	.54
4BF-8+	165	4.1	1.6	1,345	2,070	.065	1,635	2,495	.065	415	1,840	730	5	10	30.0	29.2	.23	10.0	.67
4BF-10+	165	4.1	2.0	1,395	2,295	.061	1,570	2,660	.059	410	2,000	860	3	9	29.3	26.6	.23	10.2	.62
4BF-12	165	4.1	2.8	1,735	2,930	.059	1,915	3,690	.052	390	2,810	1,520	1	4	26.5	26.5	.25	11.0	.67
4BC-8+	95	2.8	1.8	770	1,240	.062	830	1,685	.049	450	930	475	6	19	31.5	30.9	.23	10.2	.64
4BC-10+	95	2.8	2.4	675	1,425	.047	915	1,905	.048	435	880	580	5	15	30.3	30.3	.23	10.1	.64
4BC-12	95	2.8	2.4	910	2,045	.044	925	2,390	.039	415	1,140	690	1	4	30.4	26.9	.24	10.4	.64
5BF-10+	175	4.0	2.6	1,010	1,760	.057	1,750	4,370	.040	690	1,945	470	7	28	26.6	25.8	.12	5.5	.48
5BC-10+	170	2.7	2.1	1,045	1,975	.053	1,675	4,150	.040	730	1,780	405	9	32	23.4	22.9	.12	5.2	.47
6BF-10+	125	4.0	1.7	790	1,420	.055	1,230	3,035	.041	725	1,590	375	9	25	27.0	26.1	.14	6.0	.50
6BC-10+	140	2.9	1.7	940	1,835	.051	1,515	3,825	.040	745	1,945	505	4	18	23.6	22.3	.13	5.7	.49
7BF-7½	185	4.0	2.9	1,515	2,910	.052	1,655	4,000	.041	635	2,370	615	6	17	27.4	28.4	.13	5.9	.54
7BF-10+	185	4.0	3.0	1,500	3,160	.047	1,785	4,125	.043	575	2,080	670	4	15	25.1	26.4	.13	5.8	.55
7BF-12	185	4.0	3.8	1,850	3,840	.048	1,990	4,950	.040	515	2,630	790	3	10	21.1	21.7	.13	5.6	.50
7BC-7½	95	3.1	2.5	750	1,535	.049	900	2,330	.039	775	1,060	370	7	28	30.3	30.1	.13	5.6	.54
7BC-10	95	3.1	2.5	770	1,645	.047	925	2,795	.033	570	1,010	385	7	30	28.9	25.1	.14	6.3	.54
7BC-12	95	3.1	3.4	750	1,675	.045	925	2,550	.036	610	1,375	450	5	19	24.3	23.5	.13	5.9	.51

7BC–10	95	3.1	2.5	770	1,645	.047	925	2,795	.033	570	1,010	385	7	30	28.0	25.1	.14	6.3	.54
7BC–12	95	3.1	3.4	750	1,675	.045	925	2,550	.036	610	1,375	450	5	19	24.3	23.5	.13	5.9	.51
8BF–7½	125	3.9	1.6	1,645	2,380	.069	1,745	2,970	.059	500	2,000	930	5	13	30.7	30.3	.20	8.9	.61
8BF–10+	125	3.9	2.0	1,560	2,535	.062	1,755	3,240	.054	440	2,190	1,090	4	7	29.4	27.8	.22	9.9	.62
8BF–12	125	3.9	2.7	1,795	3,195	.056	1,930	3,840	.050	425	2,010	1,370	3	7	27.2	27.5	.24	10.8	.65
8BC–10	85	2.4	2.7	1,025	1,920	.053	1,100	2,185	.050	480	1,360	710	3	9	31.4	31.0	.20	8.9	.61
9BF–7½	170	4.6	2.1	1,605	2,850	.056	1,595	3,470	.046	510	2,150	600	5	14	29.6	30.5	.16	7.0	.57
9BF–10+	170	4.6	2.6	1,720	3,440	.050	1,630	3,955	.041	485	2,580	805	4	12	27.4	25.8	.15	6.8	.55
9BF–12	170	4.6	2.8	1,930	3,655	.053	1,935	4,325	.045	475	2,350	880	3	11	25.3	23.7	.16	7.0	.56
9BC–10	105	2.5	2.5	910	2,095	.044	1,050	2,575	.041	500	1,265	455	7	19	28.2	29.0	.16	7.2	.56
10BF–10+	140	3.7	2.8	1,010	1,505	.067	1,215	2,260	.054	480	2,140	735	4	13	32.4	30.2	.19	8.3	.58
10BC–9½	105	3.3	2.6	795	1,470	.053	820	1,960	.042	475	1,450	610	5	15	33.8	29.2	.21	9.0	.60
11BF–11	140	4.9	3.4	1,190	1,935	.061	1,385	2,620	.053	530	2,230	840	2	8	34.7	31.6	.18	8.1	.58
11BC–9½	100	2.6	2.5	720	1,165	.062	865	1,785	.048	525	1,115	540	5	14	34.6	30.5	.20	8.7	.59
12BF–9½	145	4.2	2.4	1,090	1,580	.069	1,355	2,275	.059	400	2,120	620	7	16	32.0	29.2	.20	8.7	.58
12BC–9½	125	3.0	2.6	875	1,470	.059	1,095	2,370	.046	410	1,420	750	4	11	31.8	27.3	.21	9.2	.59
13BF–8+	255	3.1	2.3	1,665	2,515	.066	1,855	3,080	.060	400	2,380	730	9	21	24.8	25.3	.22	9.7	.63
13BF–9½	255	3.1	2.2	1,825	2,875	.063	1,795	3,610	.050	420	2,570	920	3	7	23.7	25.3	.23	10.2	.63
13BF–12	255	3.1	3.0	2,005	3,120	.064	1,785	3,800	.047	350	2,870	970	3	6	22.6	23.0	.25	11.0	.66
13BC–7½	115	2.6	1.8	890	1,390	.064	965	2,025	.048	515	1,250	460	6	23	28.2	27.9	.22	9.9	.62
13BC–9½	115	2.6	2.7	790	1,470	.053	970	2,130	.045	535	1,110	510	5	20	27.1	27.1	.23	10.1	.61
13BC–12	115	2.6	1.8	955	1,725	.055	1,000	2,290	.044	475	1,480	630	5	16	26.0	26.2	.24	10.6	.63
14BF–8+	135	4.9	.6	890	1,055	.084	1,320	2,305	.057	665	1,530	560	5	16	34.0	33.4	.13	5.8	.52
14BF–10	135	4.9	1.7	1,000	1,320	.075	1,340	2,410	.056	775	1,465	675	2	9	32.4	34.0	.15	6.4	.51
14BF–12	135	4.9	2.4	1,100	1,610	.068	1,250	2,950	.042	625	1,805	760	3	9	31.1	31.7	.17	7.4	.57
14BC–7½	75	2.8	1.8	380	505	.075	750	795	.094	890	930	310	10	41	36.2	36.0	.15	6.7	.53
14BC–10	75	2.8	2.8	485	665	.073	785	1,030	.076	885	985	395	7	26	34.7	34.7	.15	6.8	.53
14BC–12	7.	2.8	3.0	495	770	.064	760	1,545	.049	810	1,155	420	3	17	33.3	33.8	.17	7.6	.56
15BF–9½	150	4.4	2.9	1,725	2,790	.061	1,790	3,160	.057	460	2,240	1,000	4	9	29.1	29.5	.18	8.1	.58
15BC–11	95	2.9	3.0	710	1,575	.045	1,005	2,060	.049	550	890	475	6	19	26.9	28.3	.17	7.6	.57
16BF–10½	140	4.6	2.4	1,640	3,345	.048	1,725	3,840	.045	415	1,710	825	5	14	25.4	27.5	.19	8.4	.56
16BC–9½	210	4.1	4.3	1,765	3,605	.049	1,560	3,640	.043	435	1,990	910	5	14	23.8	24.9	.18	8.0	.56
17BF–9½	140	3.9	3.1	1,405	2,050	.068	1,560	2,360	.066	550	2,050	825	2	7	32.8	32.9	.18	7.8	.57
17BC–10½	100	2.5	2.7	730	1,205	.060	800	1,975	.040	625	990	565	5	15	31.5	31.2	.18	7.8	.57
18BC–11	105	3.5	2.8	1,085	2,235	.048	1,160	2,790	.041	425	1,170	790	5	11	25.1	26.2	.20	8.7	.60
19BC–11	95	3.6	3.1	1,095	2,585	042	1,215	3,520	.034	445	880	760	4	12	23.7	23.8	.16	7.2	.54
20BC–10½	90	3.9	4.1	1,025	2,005	.051	1,145	2,695	.042	440	1,050	650	4	10	26.8	26.7	.19	8.3	.56
K–7½	100	2.3	1.2	595	930	.064	860	1,910	.045	730	790	430	9	33	31.5	30.1	.15	6.7	.57
K–10	100	2.3	2.1	580	1,290	.045	945	2,445	.039	805	935	525	4	15	29.2	29.2	.16	6.9	.55
K–12	100	2.3	2.9	710	1,440	.049	980	2,340	.042	740	1,025	610	2	11	26.8	27.2	.16	7.1	.54
L–7½	85	2.6	1.9	495	815	.060	710	1,165	.061	460	630	380	5	20	32.2	31.6	.17	7.5	.57

[1] Computed outer fiber strain or elongation $= \frac{\text{modulus of rupture}}{\text{modulus of elasticity}}$.

[2] The values given represent the average temperature resulting after testing 3 to 5 saggers.

TABLE 2.—*Properties of sagger bodies*—Continued

Body No. and cone at which fired	Modulus of rupture of unfired body	Dry shrinkage	Fired shrinkage	Tested at 20° C.			Tested at temperature at which sagger failed in quenching test				Tested at 1,000° C.		Total plastic deflection in inches (taken from plastic flow curves). Stress of approximately—		Porosity of bars	Porosity of saggers	Total expansion from atmospheric temperature to 250° C.	Coefficient of expansion atmospheric temperature to 250° C.	Total expansion from atmospheric temperature to 1,000°C.
				Modulus of—		Computed [1] outer fiber strain	Modulus of—		Computed [1] outer fiber strain	Sagger [2] failing at	Modulus of—		120 lbs./in.²	240 lbs./in.²					
				Rupture	Elasticity		Rupture	Elasticity			Rupture	Elasticity							
	Lbs./in.²	*Per cent*	*Per cent*	*Lbs./in.²*	*1,000 lbs./in.²*	*Per cent*	*Lbs./in.²*	*1,000 lbs./in.²*	*Per cent*	*°C.*	*Lbs./in.²*	*1,000 lbs./in.²*	*×10⁻⁴*	*×10⁻⁴*	*Per cent*	*Per cent*	*Per cent*	*×10⁻⁶*	*Per cent*
L-10	85	2.6	2.5	705	1,300	0.054	815	1,790	0.046	465	900	750	3	10	30.0	30.9	0.23	10.2	0.61
L-12+	85	2.6	2.4	755	1,500	.050	935	1,915	.049	435	1,090	960	2	9	27.4	28.5	.25	10.9	.63
M-7½	95	2.5	1.7	550	920	.060	710	2,035	.035	475	545	220	5	19	29.3	29.8	.21	9.3	.61
M-10	95	2.5	2.4	715	1,265	.056	855	2,160	.039	490	865	765	3	11	29.0	28.7	.21	9.5	.63
M-12+	95	2.5	3.5	755	1,620	.046	965	2,205	.044	415	905	840	5	12	26.0	26.7	.24	10.5	.67
A-9½	110	4.6	4.3	1,235	2,440	.050	1,185	3,150	.038	410	1,795	1,400	1	4	28.5	27.5	.18	7.9	.57
B-9½	85	4.6	4.4	1,095	2,325	.047	1,450	3,150	.046	435	1,615	1,195	1	4	30.5	29.7	.20	9.0	.61
C-10	90	3.2	2.8	915	1,775	.051	760	2,325	.033	635	1,155	520	2	11	26.5	25.6	.14	6.3	.51
E-10	95	3.9	2.9	825	1,240	.066	1,155	2,080	.055	485	1,490	755	5	11	32.9	31.7	.18	7.8	.57
F-9½	55	3.8	3.1	930	1,810	.051	1,200	2,285	.052	410	1,385	910	3	8	31.6	31.9	.21	8.9	.63
G-9½	55	3.4	6.6	880	2,160	.040	885	2,525	.035	435	1,290	855	2	5	30.0	30.1	.21	9.1	.59
H-9½	40	2.7	2.7	665	970	.068	1,090	2,155	.051	710	1,230	520	4	10	27.6	28.3	.17	7.5	.56

[1] Computed outer fiber strain or elongation $= \frac{\text{modulus of rupture}}{\text{modulus of elasticity}}$.

[2] The values given represent the average temperature resulting after testing 3 to 5 saggers.

The results show that the thermal expansions of the bodies change with the temperature of firing, but such changes are not consistently either in the same direction or of the same magnitude. This, naturally, must be expected because of the various types of clays used in compounding the bodies. The thermal expansion data for two typical bodies fired at three different temperatures are given in Figure 1.

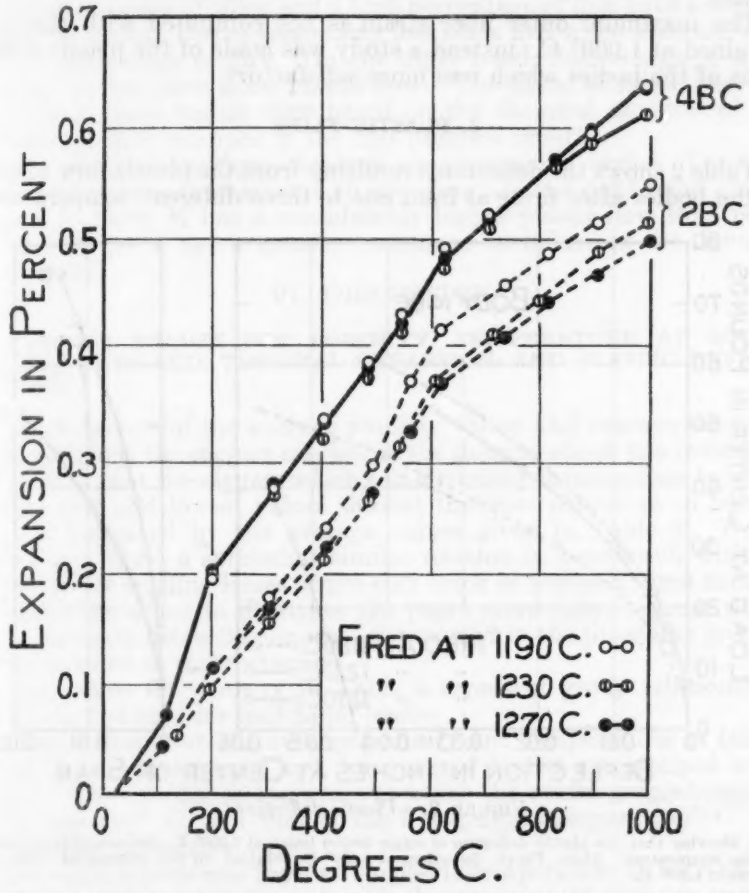

FIGURE 1.—*Showing the linear thermal expansion of two typical sagger bodies fired at three different temperatures*

The great difference in total expansion at 200° C. is well illustrated

Body 4BC shows little change in expansion when tested after firing at each of three temperatures, whereas the expansion of body 2BC decreases with increased temperature of firing. The great difference in the rate of expansion below 200° C. is very noticeable in these two bodies.

Moduli of rupture and elasticity values were obtained at three different temperatures for all bodies (two only for 1BC–8). Check determinations were made of all bodies (one only for 4BC and 20BC) at ordinary temperatures, and of 20 bodies at 1,000° C. In all cases the values obtained for any one body were within approximately 10 per cent of the mean.

The computed maximum outer fiber strain (elongation) is given for all bodies, both at room temperature and at the temperature at which the saggers failed in the thermal shock test. These values show how the elongation of the material decreases in most cases at the higher temperature. The data show that the fine-grogged bodies have a greater fiber elongation before rupture than the coarse-grogged bodies.

The maximum outer fiber strain is not computed with the data obtained at 1,000° C.; instead a study was made of the plastic deflections of the bodies which was more satisfactory.

3. PLASTIC FLOW

Table 2 shows the deflections resulting from the plastic flow of each of the bodies after firing at from one to three different temperatures.

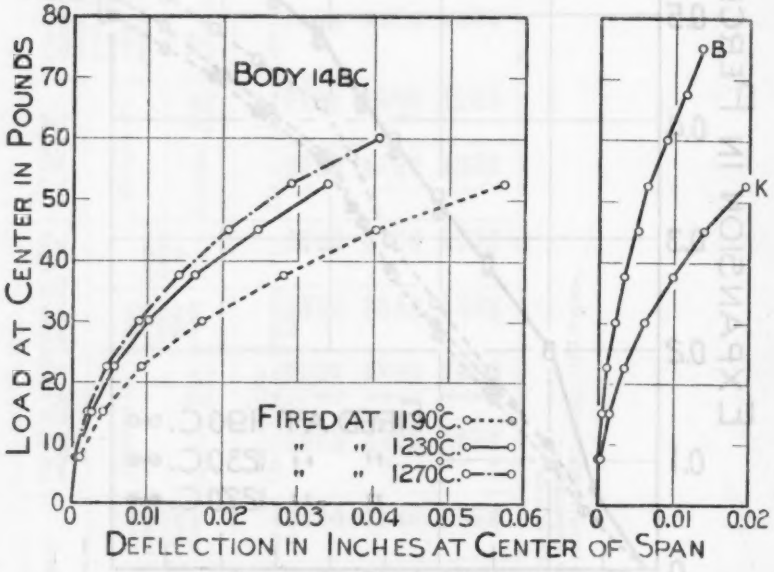

FIGURE 2.—*Plastic deflections*

Left: Showing that the plastic deflection of sagger bodies tested at 1,000° C. decreases with increase of firing temperature. Right: Plastic deflections at 1,000° C. obtained on two commercial bodies after firing at 1,230° C.

The results were obtained at 1,000° C. and represent the total plastic deflection in inches, at the end of 10 minutes with, first, a load of 120 lbs./in.^{2}, and second a load of 240 lbs./in.^{2}, applied midspan of the 1 by 1 by 12 inch specimens on a 10-inch span. Within the limits of firing temperatures and grog sizes used, the following information relative to plastic flow was obtained:

1. Bodies containing the coarser sizes of grog have a plastic flow decidedly greater than those containing the finer sizes of grog.

2. The plastic flow decreases with increase of temperature of firing of the specimens. A typical illustration of such changes is shown with body 14BC in Figure 2. Saggers fired at the lowest temperature may prove unsatisfactory in service, whereas if fired at the highest temperature may prove to be quite satisfactory. Data represented

by these curves illustrate further the undesirability of heavily loading saggers which have not been fired at sufficiently high temperatures.

3. The percentage increase in plastic flow when loads of 120 and 240 lbs./in.^{2} are used is decidedly different for the different clays.

4. The percentage flux content is an important factor in the tendency of the bodies to flow at high temperatures. Bodies containing a high percentage of silica and a high percentage of flux have a greater plastic flow than bodies containing less silica and more alumina with a high percentage of flux. On the other hand, bodies high in silica and low in flux have a low plastic flow. The silica, alumina, and flux content of these bodies were based on the chemical analyses of the individual clays reported in the first progress report.[4]

The plastic deflections obtained on commercial bodies B and K, after having been fired at cone 10, are shown in the right-hand graph. (Fig. 2.) Body K has a considerably higher plastic flow than body B, but K has a much greater resistance to failure in the thermal-shock tests.

VI. DISCUSSION

1. AVERAGE VALUES FOR POROSITY, TEMPERATURE AT WHICH SAGGERS FAILED, THERMAL EXPANSION, AND PLASTIC DEFLECTIONS

A comparison of the average porosity values and average temperatures at which the saggers cracked in the thermal-shock test indicated, in general, that the saggers which had a porosity intermediate between the highest and lowest values showed the least resistance to failure. This is indicated by the average values given in Table 3. H. G. Schurecht found a somewhat similar relation in connection with his study of the spalling losses of fire-clay brick in malleable-iron furnace linings.[5] In order to illustrate the point more fully, saggers which had a porosity below 20 per cent, as reported in the preceding report,[6] were included in these averages.

The values for porosity in Table 3 represent group relationships which do not hold for individual bodies.

Table 3 also gives the average porosity and temperatures of failure when the coarse-grogged and fine-grogged bodies are grouped separately. The average temperature at which the coarse-grogged saggers failed was 605° C. and that of the fine-grogged saggers 535° C., an appreciable difference.

The total expansions from atmospheric temperature to 250° C. are also averaged and correspond with the grouping of porosity values. The maximum expansion occurred with bodies which had a porosity of 28 per cent, and in turn fail in the thermal shock test at the lowest average temperature. A comparison of the average thermal expansion values with the average temperatures at which the saggers failed shows that a very close relation exists between these two properties.

The total plastic deflections determined at 1,000° C. with a stress of approximately 240 lbs./in.^{2} are included with the averages of other properties in Table 3. There appears to be a general relation of plastic deflection to the other properties. The average values for plastic deflection when the coarse and fine grogged bodies are sepa-

[4] See footnote 1, p. 1017.
[5] The Behavior of Fire Brick in Malleable Iron Furnaces. Trans. Am. Foundrymen's Association, Vol. 30, p. 391–94.
[6] See footnote 1, p. 1017.

rated show clearly that the coarse-grogged bodies have decidedly greater plastic flow than the fine.

TABLE 3.—*Average values of porosity, nature of grog, temperature of failure, and plastic flow of all laboratory-made sagger bodies*

Total number of bodies	Porosity [1]	Temperature at which saggers failed in thermal-shock test	Thermal expansion total at 250° C.	Total plastic deflection at 1,000° C. with a stress of approximately 240 lbs./in.²
	Per cent	*°C.*	*Per cent*	*Inches per 10-inch span*
16	19.0 (16–21.9)	600	0.110	0.00525
12	24.0 (22–25.9)	530	.170	.00175
10	26.0 (26–26.9)	500	.190	.00200
13	28.0 (27.0–29.9)	475	.200	.00150
7	30.0 (30.0–30.9)	525	.190	.00175
9	32.0 (31.0–32.9)	630	.160	.00175
7	35.0 (33.0–38.0)	800	.150	.00275
	COARSE-GROGGED BODIES ALONE			
	26.7	605	0.171	0.00240
	FINE-GROGGED BODIES ALONE			
	26.3	535	0.171	0.00143

[1] The average porosity in each case included those bodies coming within the range of porosity values given in the parentheses.

2. CORRELATION OF THERMAL EXPANSION, COMPUTED MAXIMUM OUTER FIBER STRAIN AND TEMPERATURE AT WHICH SAGGERS FAILED

In correlating the properties of the sagger bodies which were determined, it was necessary to separate the data obtained on the coarse and fine-grogged bodies because of such properties as thermal conductivity and diffusivity which were not studied and which undoubtedly are not the same in the two types of bodies. Because of the fact that several of the bodies studied were identical except for the sizes of the grog they contained and, because the coarse-grogged bodies showed the greater resistance to failure in the thermal shock test in spite of having the lower computed fiber elongation it must be assumed that the thermal conductivity and other thermal properties have an important effect on the life of the sagger.

Figures 3 (fine-grogged bodies) and 4 (coarse-grogged bodies) show the relation that thermal expansion (abscissa) and computed maximum fiber elongation (ordinate) bear to the resistance of the saggers to failure when subjected to thermal shock (vertical line). These models were made because they illustrate very clearly the importance of controlling, first the thermal expansion and, second the maximum fiber elongation if it is desired to obtain a high resistance of saggers to failure when subjected to temperature changes. Figure 3 (A), and Figure 4 (A), were taken to show the scattering of the points in the horizontal plane; Figure 3 (B), taken along the abscissa shows the increasing resistance of saggers to failure with decreasing thermal

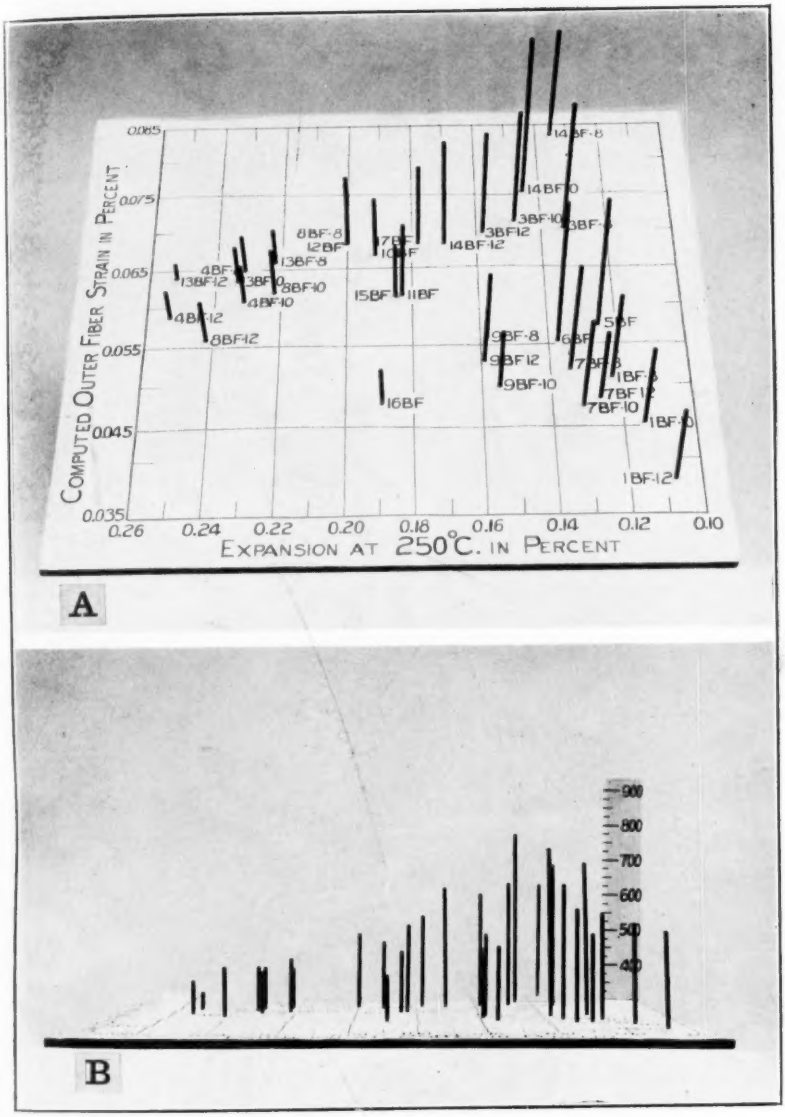

FIGURE 3.—*Three dimensional models illustrating the properties of fine-grogged sagger bodies*

A, The relation between linear thermal expansion (abscissa), computed fiber elongation (ordinate) and the resistance of saggers to failure due to thermal shock (vertical); *B*, the gradual decrease in resistance to failure due to thermal shock (indicated by the height of the pegs) is accompanied with increase of total expansion. (Read from left to right.)

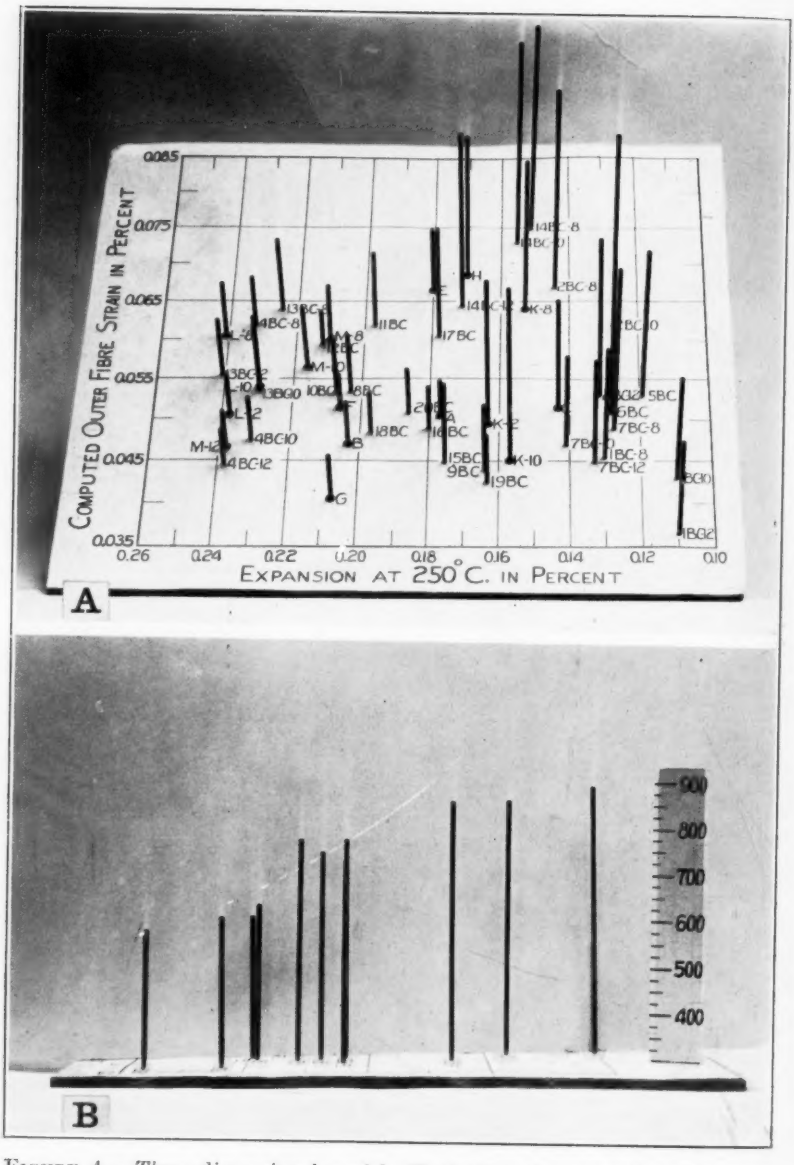

FIGURE 4.—*Three dimensional models illustrating the properties of coarse-grogged sagger bodies*

A, Similar to Figure 3(*A*); *B*, the increase in resistance to failure due to thermal shock is accompanied by increased computed fiber elongation. (Read from left to right.)

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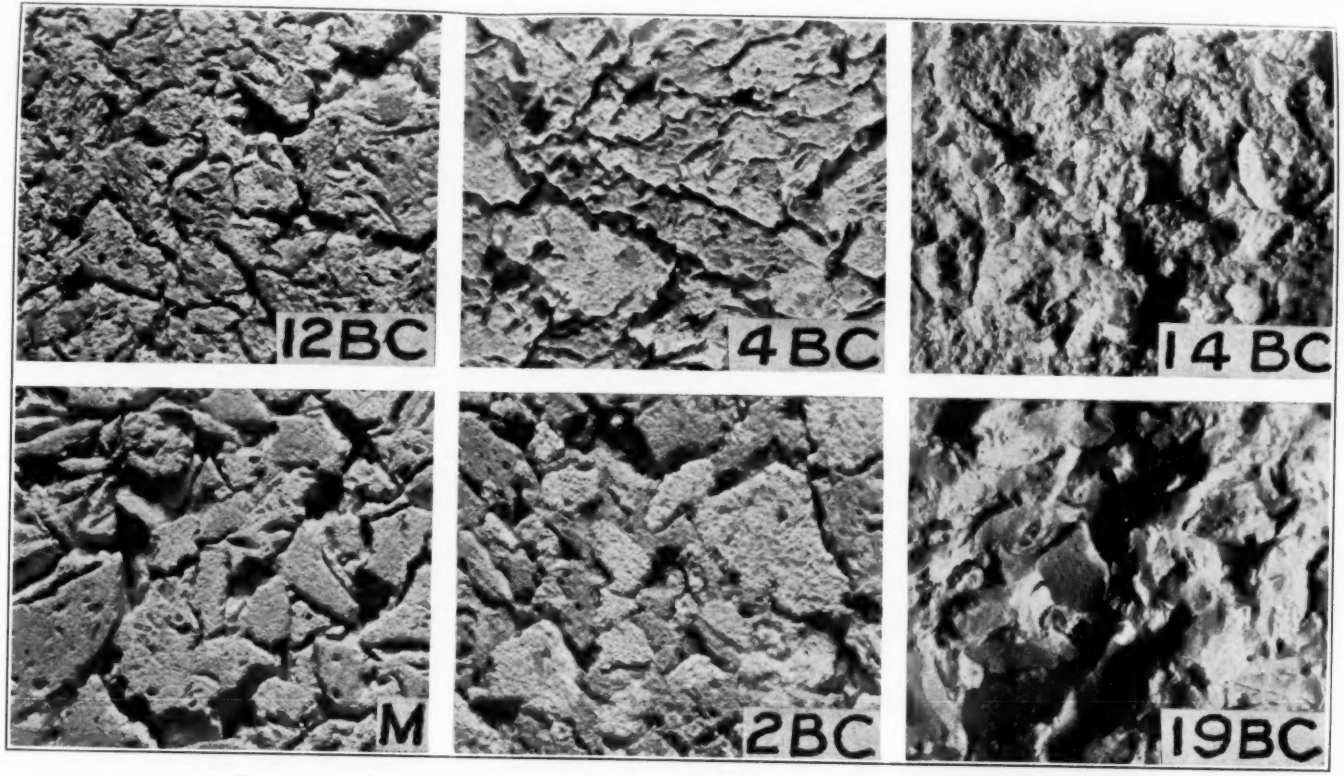

FIGURE 5.—*Photomicrograph (6 diameters) showing structure of six different sagger bodies*

expansion and Figure 4 (B), taken along the ordinate axis, indicates that if the thermal expansion is maintained within the range of 0.10 to 0.15 per cent, the bodies show greater resistance to failure, indicated by the height of the pegs, as the computed maximum fiber elongation becomes greater. The models also show that it is most important to keep the total expansion from 20° to 250° C. below 0.18 per cent, or the coefficient for this temperature range below 8×10^{-6}. The necessity for this is especially obvious from an examination of Figure 4, which shows a sharp line of demarcation from saggers having good resistance to failure to those having poor resistance at approximately the position of the line indicating a total expansion of 0.18 per cent. The models also show that the resistance of saggers to thermal shock depends more on the thermal dilatation than on the computed outer fiber strain. Furthermore, it is apparently out of the question to develop a sagger of high resistance to failure by increasing the fiber elongation as a result of change in structure of the body if the total thermal expansion from 20° to 250° C. is approximately 0.18 per cent or above.

The trend of the points is more regular in the case of the fine-grogged bodies (fig. 3) than those containing the coarse grog (fig. 4). This is partially due to the fact that the commercial bodies (pegs with circle around the base) are included with the coarse-grogged laboratory prepared bodies. The grog sizing in most of the commercial bodies is more or less haphazard. This would naturally cause some irregularity in the trend of the points. Another cause for irregularity is probably due to the fact that the percentage change in the maximum fiber elongation with increase of temperature is not the same for all bodies. Commercial body "A," Table 2, is an example of the type of body in which the fiber elongation decreases rather rapidly with increase of temperature. Consequently the saggers prepared from this body would fail at a somewhat lower temperature than might be indicated by the computed maximum fiber elongation based on results determined at room temperature and the thermal expansion data.

It is also pointed out that in spite of the care exercised in firing the ware, the temperature within the kiln was sufficiently nonuniform to account for differences in the physical properties between bar specimens and saggers though both were prepared from the same body and fired at the same time. This condition is well illustrated if the porosities of the bars and saggers are compared. Although in most instances the differences are small, attention is directed to the fact that the differences in other properties may be quite pronounced. For example the data show that a change of 10 per cent in the value for porosity due to firing at the higher temperatures might easily account for a 50 per cent change in modulus of elasticity. (Bodies 3BF, 14BF, Table 2.) In correlating the results obtained on bar specimens with those obtained on the saggers, some of the apparent discrepancies can easily be accounted for by the slight differences in firing treatment which the ware received.

3. BODY STRUCTURE

Figure 5 shows the structure of various types of sagger bodies. Body 12BC and commercial body "M" are of greatly different structure, but have very nearly the same linear thermal expansion and

maximum fiber elongation. The reasons for the poor resistance to failure shown by saggers prepared from these bodies is probably due to their comparatively high thermal expansion below 250° C. and the rapid decrease in maximum fiber elongation with increase of temperature. The grog particles in body "M" are not well bonded, but because of the angular shape of the grog which permits interlocking of the particles, a high fiber elongation is obtained. Bodies 2BC and 4BC have the same computed maximum fiber elongation, but have greatly different thermal expansion. The porosity of the grog in body 2BC is greater than that in 4BC. As a result the resistance to failure shown by body 2BC is almost twice as great as that shown by 4BC. Bodies 14BC and 19BC have a relatively low and very nearly the same thermal expansion, but the maximum fiber elongation determined at 20° C. was very much greater for 14BC than 19BC. As a result of both the favorable fiber elongation and thermal expansivity saggers prepared from body 14BC did not crack in the heat-shock test before reaching 890° C., whereas those prepared from body 19BC cracked at an average temperature of 445° C. A study of the photograph for 19BC shows that the grog used is nearly vitrified. Its effect on the structure was undoubtedly one of the primary causes of the comparatively low resistance to failure of saggers prepared from body 19BC.

Some information on the effect of resistance of saggers to failure when subjected to heat shock and when using open and dense firing clays as grog in the body compositions was given in the preceding report.[7] Additional data have been obtained, and are summarized in Table 4, to show the advantage of using open burning grog rather than the dense burning. The table is made up of five groups, the bond remains unchanged in each of the bodies of any one group, but the grog is varied. A comparison is intended between the members of a group and not between the groups.

TABLE 4.—*Temperatures of failure of saggers and porosities of clay and grog in the bodies*

Group	Body No.*	Average porosity of clays	Average porosity of grog	Temperature at which saggers cracked
		Per cent	*Per cent*	*° C.*
A	1BC	28.0	14.0	635
	2BC	28.0	32.0	865
B	10BF	33.0	33.0	480
	11BF	33.0	36.0	530
	12BF	33.0	30.0	400
C	10BC	33.0	33.0	475
	11BC	33.0	36.0	525
	12BC	33.0	30.0	410
D	15BF	31.0	31.0	460
	16BF	31.0	26.0	415
	17BF	31.0	36.0	550
E	15BC	31.0	31.0	550
	16BC	31.0	26.0	435
	17BC	31.0	36.0	625

* See Table 1 for body compositions.

[7] See footnote 1, p. 1017.

These results, as well as those previously reported, show that in every case the sagger life is increased as grog of greater porosity is used. Although the fiber elongation is favorably affected with increase of porosity in most cases there are changes in the other properties, such as thermal expansion, which materially affect their life as well.

In conclusion, it might be stated that the results of the entire study indicate that in the majority of instances it is desirable to analyze the conditions of service under which saggers are to be used. In most cases it is apparently impossible to prepare sagger bodies from the usual run of sagger clays without sacrificing one or more desirable properties for the sake of some one property which the user deems to be paramount to all others. For instance, if it is considered necessary or desirable to have a strong sagger with a low plastic deflection, it would be advisable to eliminate the coarser sizes of grog. The resistance to failure due to thermal shock would necessarily have to be sacrificed to some extent. On the other hand, where resistance to thermal failure is of primary importance and where the load is light, so that plastic deflection is of minor consideration, a coarse grogged body with a low thermal expansion should be chosen. In other words, by knowing the properties of the material entering into a body, it is possible to make saggers having properties which are considered the most desirable for the service intended and which approach the best that may be obtained with such clays.

VII. SUMMARY

From 5 to 12 small saggers were made from each of 35 laboratory prepared sagger bodies and from each of 10 commercially prepared bodies. The 35 bodies were prepared from combinations of 28 different clays, some of which were used only as the bond, others as both grog, obtained after firing, and bond. The majority of the bodies were made in two series, one of which was prepared with coarse grog and the other with fine grog. The saggers were tested for resistance to heat shock after firing at one or all three of the following temperatures, namely, 1,190°, 1,230° and 1,270° C. Specimen bars were made to correspond with each set of saggers and fired simultaneously with the saggers. These bars were used for determining linear thermal expansion from 20° to 1,000° C., porosity, moduli of elasticity and rupture and plastic flow at 1,000° C.

The data show that increases in the temperature of firing, although evidenced by comparatively small decreases in the porosity of the sagger bodies may cause great increases in the modulus of elasticity. This in turn affects the maximum fiber elongation unfavorably and thereby decreases the resistance of saggers to failure due to thermal shock.

The linear thermal expansion of the bodies changes with increase of temperature of firing, but such changes are not consistently either in the same direction or of the same magnitude.

Data are given to show the importance of controlling, first, the linear thermal expansion and, second the maximum fiber elongation if it is desired to obtain a high resistance of saggers to failure due to thermal shock. A total linear thermal expansion from 20° to 250° C. of approximately 0.18 per cent or greater practically precludes the possibility

of obtaining a sagger having a high resistance to thermal shock. The life of the sagger is more sensitive to changes in thermal expansion than to changes in the computed outer fiber elongation.

The plastic flow studies at 1,000° C. show that:

1. Bodies containing the coarse sizes of grog have plastic deflections decidedly greater than those containing the fine grog sizes.
2. The plastic flow decreases with increase of temperature of firing of the specimens.
3. The flux content is an important factor in the tendency of the bodies to flow or deform at high temperatures, and is more serious if the silica content is high.

The results show that it is very desirable to analyze the conditions of service under which saggers are to be used because in most cases it is impossible to prepare sagger bodies, from the usual run of clays, which have properties ideally suited for longevity in all types of service. By studying the properties of the finished sagger body and the clays and grog constituting it, it is possible to make quality saggers limited only by the character of the materials used.

WASHINGTON, May 29, 1931.

THERMAL EXPANSION OF HEAT-RESISTING ALLOYS: NICKEL-CHROMIUM, IRON-CHROMIUM, AND NICKEL-CHROMIUM-IRON ALLOYS

By Peter Hidnert

ABSTRACT

This paper gives data on the linear thermal expansion of various heat-resisting alloys (nickel-chromium, iron-chromium, and nickel-chromium-iron alloys). The alloys contain 0 to 77 per cent nickel, 5 to 27 per cent chromium, and 0 to 82 per cent iron.

The coefficients of expansion of the alloys were determined for various temperature ranges between 20° and 1,000° C., and the effects due to temperature, chemical composition, heat treatment, etc., were determined. Critical regions were located on the thermal expansion curves of some of the alloys.

For a given temperature range, the coefficients of expansion of nickel-chromium alloys containing from 0 to about 20 per cent chromium are nearly the same.

The effects of chromium content, carbon content, heat treatment, etc., on the coefficients of expansion of iron-chromium alloys for various temperature ranges are indicated in a figure.

The results on the thermal expansion of nickel-chromium-iron alloys were correlated with the structure of the alloys. Transformations from one phase to another caused significant changes in thermal expansion. The expansion curves on the first heating of nearly all of the cast nickel-chromium-iron alloys indicate a retardation or decrease in expansion between 700° and 800° C., due to precipitation of carbide. The effects of change of composition on the coefficients of expansion of both cast and annealed nickel-chromium-iron alloys are indicated.

The table in the summary gives a comparison of the coefficients of expansion of the three groups of alloys.

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I. INTRODUCTION

In November, 1927, after a manuscript on the thermal expansion of alloys of the "stainless iron" type [1] was completed, A. P. Spooner, engineer of tests of the Bethlehem Steel Co., Bethlehem, Pa., pointed out the many applications of the alloys of nickel and chromium for both heat and rust resisting service and suggested that it might be well for the National Bureau of Standards to consider some work on the thermal expansion of these compositions in the same manner in which the work on stainless iron had been carried out. In accordance with this suggestion, an investigation on the thermal expansion of such alloys was planned.

[1] P. Hidnert and W. T. Sweeney, B. S. Sci. Paper No. 570 1928.

The bureau secured 35 commercial heat-resisting alloys of various types through the cooperation of 10 companies.[2] The alloys supplied by these companies contain 0 to 77 per cent nickel, 5 to 27 per cent chromium, 0 to 82 per cent iron, and other elements generally in small amounts. The alloys were divided into three groups: Nickel-chromium alloys, iron-chromium alloys, and nickel-chromium-iron alloys.

The coefficients of expansion of the alloys were determined for various temperature ranges between 20° and 1,000° C., and the effects due to temperature, chemical composition, heat treatment, etc., were determined. Critical regions were located on the thermal expansion curves of some of the alloys. These data will be useful to physicists, engineers, metallurgists, and others in the application of these alloys;

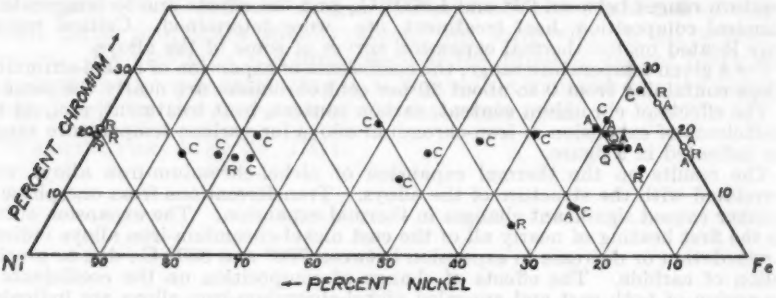

FIGURE 1.—*Portion of ternary diagram showing the chemical composition of the heat-resisting alloys investigated*

□=Ni-Cr. ○=Fe-Cr. ●=Ni-Cr-Fe.
A=Annealed. C=Cast. Q=Quenched. R=Hot-rolled.

for example, in the design of equipment for modern high-temperature processes.

II. MATERIALS INVESTIGATED

Thirty-five samples of various heat-resisting alloys (nickel-chromium, iron-chromium, and nickel-chromium-iron alloys) were investigated. Table 1 gives the commercial names, chemical compositions, heat treatments, names of manufacturers, etc. The relative locations of these samples on the ternary diagram of the nickel-chromium-iron system are shown in Figure 1. Three of the samples are binary nickel-chromium alloys, 6 are binary iron-chromium, and the remaining 26 samples are ternary alloys.

The samples used for thermal expansion determinations were approximately 299 mm in length and 6 to 13 mm in diameter (or diagonal if square or rectangular cross section).

[2] The author wishes to express his appreciation for the cooperation by Bethlehem Steel Co., Bethlehem, Pa.; Calorizing Co., Pittsburgh, Pa.; Cyclops Steel Co., Titusville, Pa.; Driver-Harris Co., Harrison, N. J.; Gilby Wire Co., Newark, N. J.; Hoskins Manufacturing Co., Detroit, Mich.; Ludlum Steel Co., Watervliet, N. Y.; Michiana Products Corporation, Michigan City, Ind.; Ohio Steel Foundry Co., Lima, Ohio; and Republic Steel Corporation, Youngstown, Ohio. These companies furnished the samples of heat-resisting alloys and information about the preparation.

TABLE 1.—*Chemical composition and heat treatment of heat-resisting alloys*

(a) NICKEL-CHROMIUM ALLOYS

Sample	Commercial name	Chemical composition [1]										Heat treatment [2]	Manufacturer	Remarks by manufacturer
		Nickel	Chromium	Iron	Manganese	Silicon	Carbon	Aluminum	Copper	Phosphorus	Sulphur			
		Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*			
1292 [3]	Chromel A	77.0	19.3	0.65	2.50	0.12	0.08	<0.1	<0.1			Hot-rolled and allowed to cool slowly	Hoskins Manufacturing Co.	Used as heating elements for high-temperature furnaces or other heating devices.
1293	Nichrome IV	[4] 76.80	20.40	.40	1.92	.26	.12		.10			Hot-rolled	Driver-Harris Co	
1402 [3]	Tophet A	77.0	19.6	.45	2.14	.13	.13	<.1	<.1			do	Gilby Wire Co	

(b) IRON-CHROMIUM ALLOYS

1294	Climet	0.00	24.63	[4] 74.08	0.62	0.27	0.16		0.24			Hot-rolled	Driver-Harris Co	
1299	Calite S	Trace.	17.04	81.74	.28	.62	.04	0.08	.14			do	Calorizing Co	Immunity from oxidation up to 1,650° F. N weather corrosion or by corrosion with nitr compounds, alkaline solutions, and many Do.
1300	do	.01	17.08	81.74	.45	.58	.06	.08				Annealed for 30 minutes at 1,450° F. and air cooled.	do	
1300A [3]	do													
1427 [6]	Stainless iron type C 2	.08	17.6	[4] 81.7	.29	.28	.04			0.021	0.021	Annealed at 1,450° F. and cooled in furnace.	Bethlehem Steel Co	
1428 [6]	No.74 heat-resisting steel	.07	24.6	[4] 74.0	.27	.29	.74			.014	.017	Annealed at 1,680° F. and cooled in furnace.	do	

(c) NICKEL-CHROMIUM-IRON ALLOYS

1291 [3]	Alloy 502	40.3	21.1	[4] 34.6	1.43	1.91	0.44	<0.1	0.1			Cast in green or bake sand at 2,550° to 2,700° F.	Hoskins Manufacturing Co.	Used very extensively in the heat-resisting f of castings, such as furnace rails, pots, an
1295		27.78	18.50	50.30	.83	1.90	.58	.08				Cast at about 2,750° F	Calorizing Co	Intended for general heat enduring appl 2,000° F. Resistant to corrosion in contac products of combustion.
1296	Calite B	8.41	21.66	64.63	1.16	1.24	1.15	1.57	.10			do	do	Intended for heat enduring applications Developed for the fabrication of beams required to sustain loads at high tem sistant to corrosion in contact with ordin combustion.
1296A [6]														
1297	Calite E	7.80	17.28	73.62	.45	.28	.14	.18	.14			Hot-rolled and cooled in brine. Annealed at 2,000° F. for 1 hour and air cooled.	do	Immunity from oxidation up to 1,800° F. weather corrosion, sulphur compound organic and inorganic salts.
1298	Calite N	58.07	19.12	19.21	.94	1.69	.54	.63	.13			Cast at about 2,750° F	do	Immune to oxidation up to 2,000° F.
1301	No. 1 alloy	65.22	16.23	15.33	1.40	1.18	.59					Cast	Michiana Products Corporation.	For high temperature.
1302	No. 2 alloy	41.98	12.12	44.10	.55	.81	.43					do	do	For medium temperature not in excess of 1,
1303 [7]	No. 4 alloy	19.80	7.76	69.30	.32	1.03	.49					do	do	
1304 [8]	Fahrite N-1	36.0	16.4	[4] 45.4	.71	1.03	.42					Cast in sand mold at 2,850° to 2,900° F.	Ohio Steel Foundry	Distinguished for its resistance to oxidatio and its unusually great strength at elevat Recommended principally for the follo ing boxes, retorts, furnace parts, disks for furnaces, domestic and industrial oil burn tube supports, and all parts used in temp from 1,000° to 2,200° F.
1305	Nichrome	61.00	15.70	[4] 20.26	.62	.69	.95		.78			Cast at about 2,750° F	Driver-Harris Co	
1306	Chromax	19.55	19.55	[4] 58.93	.15	.09	1.25		.48			Cast at about 2,825° F	do	
1306A [5]														
1310 [8]	Cyclops 17A	20.2	7.9	[4] 69.6	.74	1.12	.39					Forged at 2,050° to 1,800° F. under a hammer from an 8-inch square ingot to ¾ inch square; annealed at 1,600° to 1,650° F.	Cyclops Steel Co	
1311 [8]	Uniloy-special 18-8	9.7	19.7	[4] 69.3	.24	.89	.21					do	do	
1312 [8]	Uniloy 21-12	10.4	20.7	[4] 67.5	.62	.56	.18					do	do	
1313 [8]	Cast chromel	70.1	16.3	6.6	3.23	2.51	.94	<.1	<.1			Cast in green sand at about 2,700° F	Hoskins Manufacturing Co.	
1314 [6]	Fahrite CS	1.3	26.7	[4] 70.0	.57	.66	.72					Cast in sand mold at 2,850° to 2,900° F.	Ohio Steel Foundry Co	
1314A [5]														
1403 [6]	Tophet C	63.0	15.9	[4] 18.1	2.14	.78	.08			0.013		Hot-rolled	Gilby Wire Co	
1404 [6]	Chromin D	30.1	4.9	[4] 63.9	.64	.22	.20			.013		do	do	
1411 [9 10]	Special CNS Steel	7.5	14.0	[4] 74.7	.17	2.40	.30			.014	0.012	do	Ludlum Steel Co	Valve steel.
1411A [5]														
1418 [9 11]	Enduro KA2 Mo	8.9	17.5	[4] 69.6	.41	.37	.12			.017	.016	Hot-rolled and annealed	Republic Steel Corporation	Chief application for sulphite pulp mill eq
1419	Nirosta KA-2	10.80	17.34	[4] 71.19		.61	.06					Quenched in water from approximately 2,000° F.	Ludlum Steel Co	
1424 [9]	Nirosta KA-2S	9.6	17.7	[4] 72.0	.36	.28	.06			.016	.012	Quenched in water from 1,975° F	do	

[1] All values for chemical composition, were obtained by manufacturers on specimens cut from the ends of the investigated samples, except those indicated otherwise.
[2] Information furnished by manufacturer.
[3] Chemical analysis by J. C. Redmond, of the Bureau of Standards.
[4] By difference.
[5] Duplicate sample.
[6] Chromium and carbon contents determined by J. C. Redmond, of the Bureau of Standards. Contents of other elements from manufacturer's heat analysis.
[7] Vanadium 0.46 per cent.
[8] Nickel, chromium, and carbon contents determined by J. Redmond, of the Bureau of Standards.
[9] Nickel, chromium, and carbon contents determined by J. Redmond, of the Bureau of Standards. C elements from manufacturer's heat or ladle analysis.
[10] Tungsten 0.89 per cent.
[11] Molybdenum 3.08 per cent.

eatment of heat-resisting alloys

ALLOYS

Heat treatment [3]	Manufacturer	Remarks by manufacturer
and allowed to cool slowly	Hoskins Manufacturing Co.	Used as heating elements for high-temperature electric furnaces or other heating devices.
	Driver-Harris Co.	
	Gilby Wire Co.	

ALLOYS

	Driver-Harris Co.	
	Calorizing Co.	Immunity from oxidation up to 1,650° F. Not affected by weather corrosion or by corrosion with nitric acid, sulphur compounds, alkaline solutions, and many organic acids.
for 30 minutes at 1,450° F. cooled.	do	Do.
at 1,450° F. and cooled in	Bethlehem Steel Co.	
at 1,680° F. and cooled in	do	

RON ALLOYS

reen or bake sand at 2,550° F.	Hoskins Manufacturing Co.	Used very extensively in the heat-resisting field for all kinds of castings, such as furnace rails, pots, and supports.
out 2,750° F	Calorizing Co.	Intended for general heat enduring applications up to 2,000° F. Resistant to corrosion in contact with ordinary products of combustion.
	do	Intended for heat enduring applications up to 1,800° F. Developed for the fabrication of beams and other parts required to sustain loads at high temperatures. Resistant to corrosion in contact with ordinary products of combustion.
d and cooled in brine. Annat 2,000° F. for 1 hour and led.	do	Immunity from oxidation up to 1,800° F. Not affected by weather corrosion, sulphur compounds, and many organic and inorganic salts.
bout 2,750° F	do	Immune to oxidation up to 2,000° F.
	Michiana Products corporation.	For high temperature.
	do	For medium temperature not in excess of 1,900° F.
	do	
and mold at 2,850° to 2,900° F.	Ohio Steel Foundry	Distinguished for its resistance to oxidation and corrosion and its unusually great strength at elevated temperature. Recommended principally for the following: Carbonizing boxes, retorts, furnace parts, disks for open annealing furnaces, domestic and industrial oil burning equipment, tube supports, and all parts used in temperatures ranging from 1,000° to 2,200° F.
bout 2,750° F	Driver-Harris Co.	
bout 2,825° F	do	
t 2,050° to 1,800° F. under a er from an 8-inch square ingot nch square; annealed at 1,600° 0° F.	Cyclops Steel Co.	
	do	
	do	
reen sand at about 2,700° F.	Hoskins Manufacturing Co.	
and mold at 2,850° to 2,900° F.	Ohio Steel Foundry Co.	
ed	Gilby Wire Co.	
	do	
	Ludlum Steel Co.	Valve steel.
ed and annealed	Republic Steel Corporation.	Chief application for sulphite pulp mill equipment.
ed in water from approxiy 2,000° F.	Ludlum Steel Co.	
ed in water from 1,975° F.	do	

anadium 0.46 per cent.
ickel, chromium, and carbon contents determined by J. C. Redmond, of the Bureau of Standards.
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ungsten 0.89 per cent.
olybdenum 3.08 per cent.

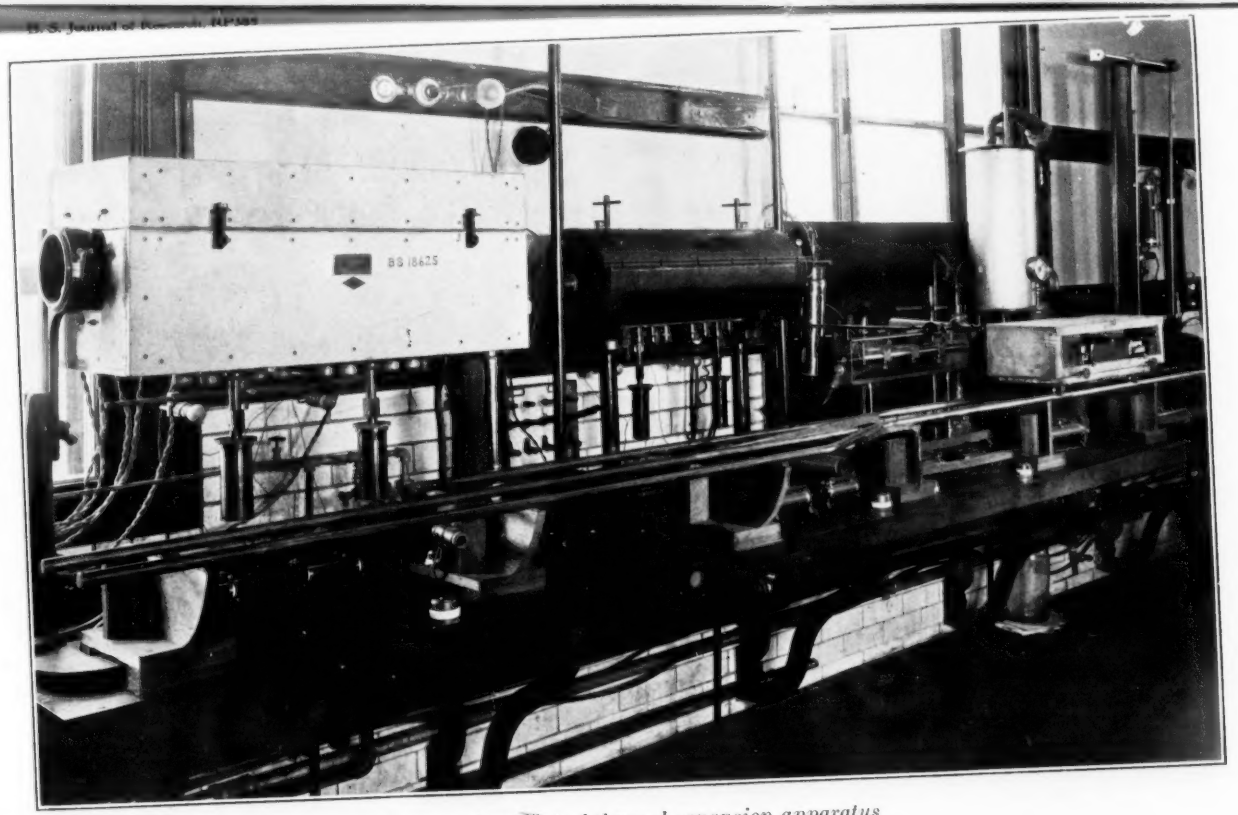

FIGURE 2.—*Part of thermal expansion apparatus*

III. APPARATUS

Figure 2 shows part of the apparatus used in this investigation. With this equipment it is possible to determine the linear thermal expansion of solids at various temperatures between −150° and +1,000° C.

The white furnace shown at the left of Figure 2 was used for temperature ranges between room temperature and 1,000° C. This furnace was employed in the tests on all of the alloys in this investigation (except the third test on sample 1296A). The observation wires were suspended from sharp V grooves near the ends of the sample

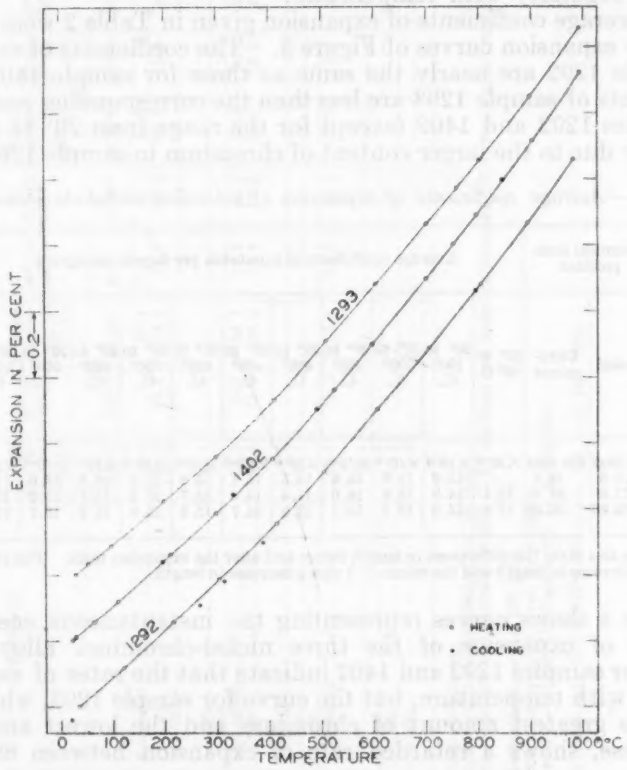

FIGURE 3.—*Linear thermal expansion of three hot-rolled nickel-chromium alloys*

1292, Ni 77.0, Cr 19.3, Mn 2.50, C 0.80, Fe 0.65, Si 0.12, Al < 0.1 Cu < 0.1 per cent.
1402, Ni 77.0, Cr 19.6, Mn 2.14, C 0.13, Fe 0.45, Si 0.13, Al < 0.1 Cu < 0.1 per cent.
1293, Ni 76.80, Cr 20.40, Mn 1.92, C 0.12, Fe 0.40, Si 0.26, Cu 0.10 per cent.

as shown in Figure 5 of Scientific Paper of the Bureau of Standards No. 524. This publication gives a detailed description of the apparatus.

IV. EXPERIMENTAL AND DERIVED RESULTS

The 35 samples of heat-resisting alloys were classified into three groups as indicated in Section II. In all cases the coefficients of expansion were derived from the observations on heating except when

indicated otherwise. The expansion curves in some figures are plotted from different origins to display the individual characteristics of each curve.

1. NICKEL-CHROMIUM ALLOYS

In this group there are three samples of hot-rolled nickel-chromium alloys containing 77 per cent nickel and about 2 per cent manganese. The chemical composition, heat treatment, and other information about the samples have been given in Table 1.

Figure 3 shows the observations obtained on the three samples of nickel-chromium alloys. The linear thermal expansion appears to increase regularly with temperature.

The average coefficients of expansion given in Table 2 were derived from the expansion curves of Figure 3. The coefficients of expansion of sample 1292 are nearly the same as those for sample 1402. The coefficients of sample 1293 are less than the corresponding coefficients of samples 1292 and 1402 (except for the range from 20° to 60° C.), probably due to the larger content of chromium in sample 1293.

TABLE 2.—*Average coefficients of expansion of hot-rolled nickel-chromium alloys*[1]

Sample	Chemical composition		Average coefficients of expansion per degree centigrade											Change in length due to heat treatment received during test
	Nickel	Chromium	20° to 60° C.	20° to 100° C.	20° to 200° C.	20° to 300° C.	20° to 400° C.	20° to 500° C.	20° to 600° C.	20° to 700° C.	20° to 800° C.	20° to 900° C.	20° to 1,000° C.	
	Per cent	*Per cent*	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$	*Per cent*
1292	77.0	19.3	------	13.6	14.0	14.3	14.5	15.1	15.6	16.1	16.5	17.0	17.6	−0.02
1402	77.0	19.6	13.1	13.3	13.8	14.0	14.4	15.0	15.7	16.2	16.7	17.2	17.8	+.00
1293	76.80	20.40	13.8	13.0	13.3	13.3	13.9	14.7	15.3	15.8	16.2	16.7	17.2	

[1] This table also gives the differences in length before and after the expansion tests. The plus (+) sign indicates an increase in length and the minus (−) sign a decrease in length.

Figure 4 shows curves representing the instantaneous coefficients or rates of expansion of the three nickel-chromium alloys. The curves for samples 1292 and 1402 indicate that the rates of expansion increase with temperature, but the curve for sample 1293, which contains the greatest amount of chromium and the lowest amount of manganese, shows a retarded rate of expansion between 600° and 800° C.

Table 3 gives a summary of the coefficients of expansion obtained by various observers, including the values obtained by the present author. These coefficients of expansion refer to various nickel-chromium alloys containing from 0 to 80 per cent chromium. The treatments (cast, wrought, hot rolled and annealed) are indicated in the table. Coefficients of expansion obtained by Hidnert [3] on nickel are included in the table. For a given temperature range, the coefficients of expansion of alloys containing from 0 to about 20 per cent chromium are nearly the same.

[3] P. Jordan and W. H. Swanger, B. S. Research Paper No. 257; 1930.

TABLE 3.—*Summary of coefficients of expansion of nickel-chromium alloys*

TABLE 3.—*Summary of coefficients of expansion of nickel-chromium alloys*

Sample	Chemical composition		Treatment	Average coefficients of expansion per degree centigrade										Observer
	Nickel	Chromium		Room temperature to 100° C.	20° to 200° C.	Room temperature to 300° C.	20° to 400° C.	20° to 500° C.	Room temperature to 600° C.	20° to 700° C.	20° to 800° C.	20° to 900° C.	20° to 1,000°C.	
	Per cent	*Per cent*		$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$	$\times 11^{-6}$	
2806F	100		Cast	14.9									[1] 17.6	Dean.[2]
B-2	99.94		Annealed [3]	13.3		14.4			15.5			16.3		Hidnert.[4]
[5]		10		13.3	13.8	14.2	14.6	15.0	15.5	15.9	16.4	16.8		Chevenard.[5]
	85	15	Wrought	[7] 13.2										[6].
	85	15	....do	[7] 13.5										[6].
	85	15	....do										16	[6].
1292	77.0	19.3	Hot-rolled	13.6	14.0	14.3	14.5	15.1	15.6	16.1	16.5	17.0	17.6	Hidnert.[8]
1402	77.0	19.6	....do	13.3	13.8	14.0	14.4	15.0	15.7	16.2	16.7	17.2	17.8	Do.[9]
	80	20	Wrought	[7] 13.2										[6].
	80	20	....do	[7] 13.5										[6].
	80	20	....do										16	[6].
1293	76.8	20.4	Hot-rolled	13.0	13.3	13.3	13.9	14.7	15.3	15.8	16.2	16.7	17.2	Hidnert.[9]
2833F	74.7	23.8	Cast	13.5									[1] 17.7	Dean.[2]
2834F	50.5	47.7	....do	13.5									[1] 17.7	Do.[2]
2835F	25	75	....do	10.3									[1] 13.1	Do.[2]
2852F	20	80	....do	8.9									[1] 12.4	Do.[2]

[1] Computed in 1931 from the published data of observer.
[2] Rensselaer Polytechnic Institute, Engineering and Science Series, No. 26; 1930.
[3] Before expansion determinations were made, sample was annealed at 950° C. for one hour and cooled in furnace. (This fact was not reported in publication mentioned in footnote 4.)
[4] L. Jordan and W. H. Swanger, B. S., Research Paper No. 257; 1930.
[5] Coefficients of expansion computed in 1931 from equation given by observer.
[6] Comptes Rendus, vol. 164, p. 916; 1917; and Revue de Métallurgie, vol. 14, p. 610; 1917.
[7] From 0 to 100° C.
[8] Data furnished by manufacturer of alloy (Proc. Am. Soc. Testing Materials, vol. 24, p. 189; 1924).
[9] Present investigation.

2. IRON-CHROMIUM ALLOYS

In the present investigation six samples of iron-chromium alloys containing from 17.0 to 24.6 per cent chromium were used. The chemical composition, heat treatment, and other information about these samples have been given in Table 1.

Figures 5 to 9, inclusive, show the observations obtained. Slight transformations were located on all samples except samples 1299 and 1294. The arrows in Figures 6 to 8 indicate the beginning of the

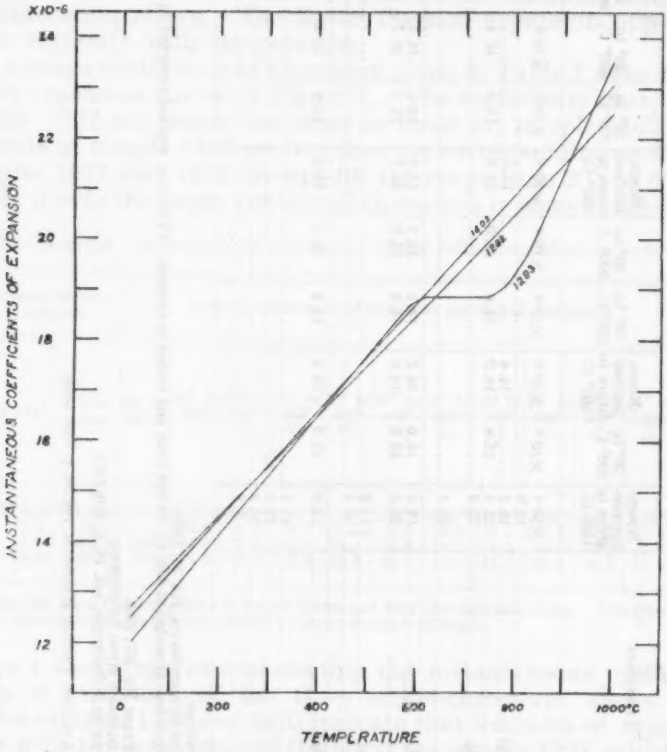

FIGURE 4.—*Instantaneous coefficients of expansion of three hot-rolled nickel-chromium alloys*

transformation. The dotted portions of the curves of samples 1299 and 1294 indicate that sufficient observations were not obtained between 900° and 1,000° C. to determine the presence or absence of transformations.

One of the following temperatures may be taken for the temperature of the beginning of the transformation or critical region on heating:

1. The temperature at which the rate of expansion (or instantaneous coefficient of expansion) of the sample begins to decrease.

2. The temperature at which the sample begins to contract. (At this temperature the rate of expansion is generally zero.)

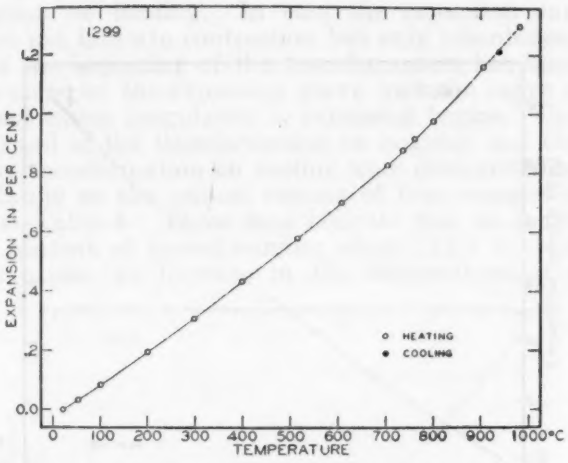

FIGURE 5.—*Linear thermal expansion of hot-rolled iron-chromium alloy*

Fe 81.74, Cr 17.04, C 0.04, Mn 0.28, Si 0.62, Ni trace, Al 0.08, Cu 0.14 per cent.

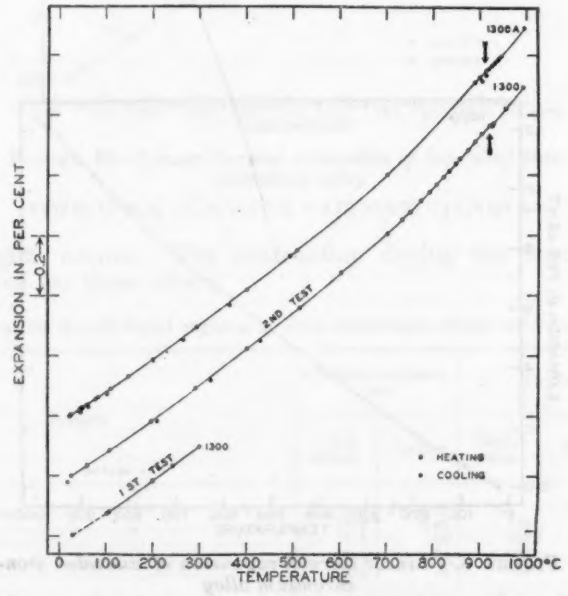

FIGURE 6.—*Linear thermal expansion of two samples of annealed iron-chromium alloy*

Fe 81.74, Cr 17.08, C 0.06, Mn 0.45, Si 0.58, Ni 0.01, Al 0.08 per cent.

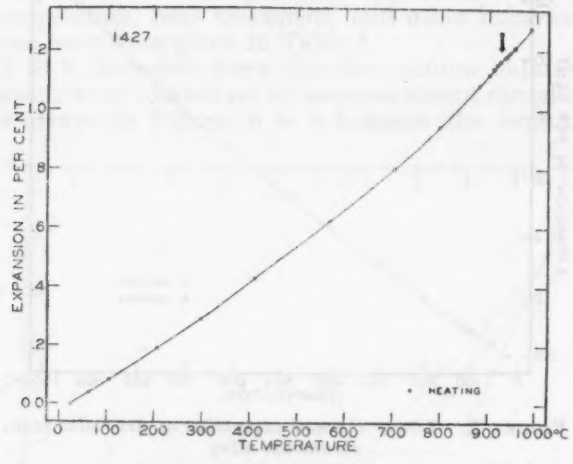

FIGURE 7.—*Linear thermal expansion of annealed iron-chromium alloy*

Fe 81.7, Cr 17.6, C 0.04, Mn 0.29, Si 0.28, Ni 0.08, P 0.021, S 0.021 per cent.

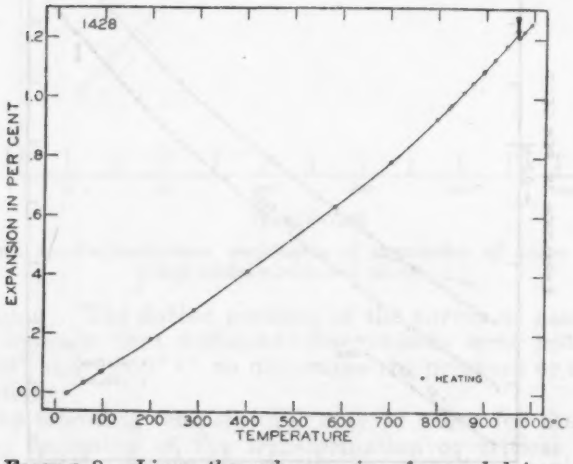

FIGURE 8.—*Linear thermal expansion of annealed iron-chromium alloy*

Fe 74.0, Cr 24.6, C 0.74, Mn 0.27, Si 0.29, Ni 0.07, P 0.014, S 0.017 per cent.

In this and preceding publications, the author has generally selected the second temperature for the temperature of the beginning of the transformation on heating. In case the expansion curve of the sample does not indicate contraction but only retardation, the temperature of the beginning of the transformation has been taken as the temperature on the expansion curve (not the curve of the rate of expansion) where irregularity in expansion begins. The temperature of the end of the transformation on heating, and the temperatures of the transformation on cooling were determined similarly.

Data relating to the critical regions of four samples on heating are given in Table 4. These data indicate that an increase in the chromium content of iron-chromium alloys (17.1 to 24.6 per cent chromium) causes an increase in the temperature at which the

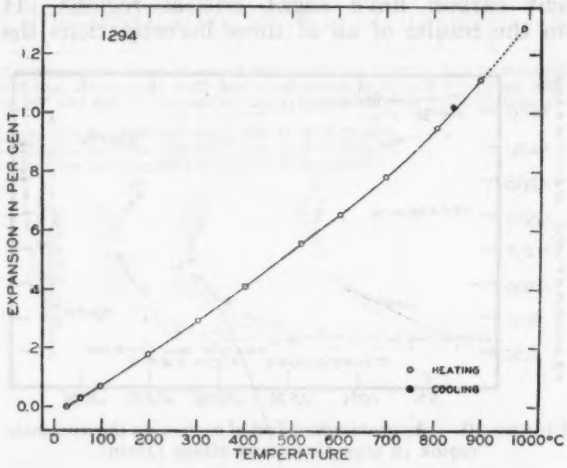

FIGURE 9.—*Linear thermal expansion of hot-rolled iron-chromium alloy*

Fe 74.08, Cr 24.63, C 0.16, Mn 0.62, Si 0.27, Ni 0.00, Cu 0.24 per cent.

critical region occurs. The contraction during the transformation is very small for these alloys.

TABLE 4.—*Critical regions of iron-chromium alloys on heating*

Sample	Chemical composition		Critical region		
	Chromium	Carbon	Beginning	End	Contraction
	Per cent	*Per cent*	*°C.*	*°C.*	*Per cent*
1300 [1]	17.1	0.06	918	924	0.002
1300A	17.1	.06	910	(?)	.000
1427	17.6	.04	925	930	.000
1428	24.6	.74	964	970	.005

[1] Second test.

The critical regions are due to transformations from alpha phase into gamma phase (austenite). Bain [4] showed a diagram (fig. 10)

[4] E. C. Bain, Transactions of American Society for Steel Treating, vol. 9, p. 9; 1926.

of the austenite region in iron-chromium alloys at elevated temperatures. The diagram indicates the approximate effect of carbon in extending the austenite region into the richer chromium alloys. This diagram may assist in correlating the apparently conflicting results of various observers. Data by Ruf[5] and Kinzel[6] indicate that the austenite region extends to about 12 per cent chromium for iron-chromium alloys containing negligible amounts of carbon. Matsushita[7] found critical regions on iron-chromium alloys containing from 0 to 20 per cent chromium and 0.6 per cent carbon. The present investigation clearly shows that an iron-chromium alloy containing 24.6 per cent chromium and 0.74 per cent carbon undergoes a transformation from the alpha to the gamma phase and that alloys containing about 17 per cent chromium and about 0.05 per cent carbon have slight critical regions. It therefore appears from the results of all of these investigations that for iron-

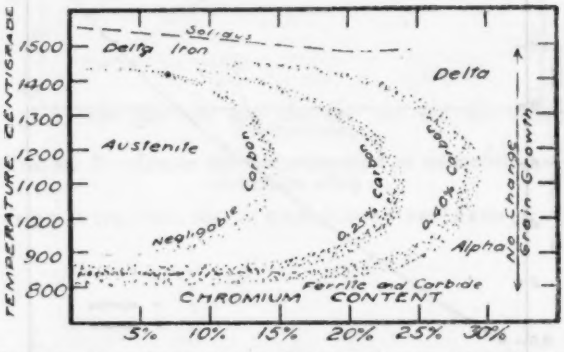

FIGURE 10.—*Approximate effect of carbon on the austenite region in iron-chromium alloys (Bain)*

chromium alloys containing negligible carbon the austenite region extends from 0 to about 12 per cent chromium, for alloys containing about 0.05 per cent carbon the region extends from 0 to at least 17 per cent chromium, and for alloys containing larger contents of carbon the austenite region is extended to higher chromium contents.

The average coefficients of expansion given in Table 5 were derived from the expansion curves of Figures 5 to 9, inclusive. The table shows that the coefficients of expansion increase gradually with temperature. The coefficients of expansion indicate a tendency to decrease slightly with increase in the chromium content of the iron-chromium alloys containing from 17.0 to 24.6 per cent chromium.

Table 6 gives a summary of the coefficients of expansion obtained by various observers, including the values obtained by the present author. These coefficients of expansion refer to various iron-chromium alloys containing from 0 to 60 per cent chromium and from 0 to 6.7 per cent carbon. The treatments (cast, annealed, quenched, etc.) are indicated in the table.

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[5] K. Ruf, Zeitschrift für Elektrochemie, vol. 34, p. 813; 1928.
[6] A. B. Kinzel, Heat Treating and Forging, vol. 14, p. 372; 1928.
[7] T. Matsushita, Science Reports Tôhoku Imperial University (first series), vol. 9, p. 243; 1920.

TABLE 5.—*Average coefficients of expansion of iron-chromium alloys*

Sample	Chemical composition		Heat treatment	Average coefficients of expansion per degree centigrade										Change in length due to heat treatment received during test
	Chromium	Carbon		20° to 60° C.	20° to 100° C.	20° to 200° C.	20° to 300° C.	20° to 400° C.	20° to 500° C.	20° to 600° C.	20° to 700° C.	20° to 800° C.	20° to 900° C.	
	Per cent	*Per cent*		$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$	*Per cent*
1299	17.0	0.04	Hot-rolled	10.3	10.6	10.8	11.1	11.4	11.7	11.9	12.1	12.5	13.1	-------
1300[1]	17.1	.06	Annealed	10.2	10.3	10.7	11.0	11.2	11.4	11.7	11.9	12.4	12.9	−0.01
1300A[2]	17.1	.06	---do	10.2	10.3	10.5	10.9	11.1	11.3	11.5	11.8	12.3	12.9	+.00
1427[3]	17.6	.04	---do	9.7	10.1	10.4	10.7	11.1	------	11.6	11.8	12.2	12.8	-------
1428[4]	24.6	.74	---do	10.5	10.2	10.5	10.7	11.0	------	11.4	11.6	12.0	12.5	-------
1294	24.6	.16	Hot-rolled	10.3	10.0	10.3	10.6	10.9	11.2	11.3	11.6	12.2	12.7	-------

[1] Coefficients of expansion obtained on second test; coefficient of expansion between 925° and 1,000° C. is 19.0×10^{-6}. On first test, the average coefficient of expansion is 10.9×10^{-6} between 100° and 200° C. and 11.6×10^{-6} between 200° and 300° C.; on cooling, the avarage coefficient of contraction is 10.9×10^{-6} between 300 and 20° C.

[2] Coefficient of expansion between 925° and 1,000° C. is 18.2×10^{-6}.

[3] Coefficient of expansion between 925° and 1,000° C. is 17.9×10^{-6}.

[4] Coefficient of expansion between 20° and 950° C. is 12.8×10^{-6}.

TABLE 6.—*Summary of coefficients of expansion of iron-chromium alloys*

Sample	Chemical composition		Treatment	Average coefficients of expansion per degree centigrade											Observer
	Chromium	Carbon		Room temperature to 100° C.	Room temperature to 200° C.	0° to 250° C.	Room temperature to 300° C.	Room temperature to 400° C.	Room temperature to 500° C.	Room temperature to 600° C.	Room temperature to 700° C.	Room temperature to 800° C.	Room temperature to 900° C.	Room temperature to 1,000° C.	
	Per cent	*Per cent*		$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$	
S507	0.0	0.02	Annealed	12.0			13.3			14.7					Souder and Hidnert.[1]
	0	(2)	Cast			[3] 12.6									Ruf.[4]
2811F [5]	0	<.1	do	13.3										17.8	Dean.[6]
S482	0.19	1.28	Annealed	11.0			12.0			14.1					Souder and Hidnert.[1]
S552	.57	.36	do	11.8	[7] 12.3		13.1	[7] 13.6	[7] 14.1	14.5	[7] 14.9				Do.[1]
1,223	.78	.40	Quenched and drawn	12.8	[7] 13.4										Hidnert.[6]
S560	.82	.34	Annealed	11.6	[7] 12.1		12.9	[7] 13.7	[7] 14.2	14.6	[7] 14.9				Souder and Hidnert.[1]
S558	.85	.12	do	11.6	[7] 12.1		12.7	[7] 13.2	[7] 13.6	14.0	[7] 14.3				Do.[1]
S557	.92	.17	do	11.3	[7] 11.6		12.5	[7] 13.2	[7] 13.7	14.2	[7] 14.5				Do.[1]
1,048	.96	.34	Quenched and drawn	11.8	[7] 12.7										Hidnert.[6]
S546	1.00	.35	Annealed	12.4	[7] 12.6		13.3	[7] 13.8	[7] 14.2	14.5	[7] 14.7				Souder and Hidnert.[1]
S555	1.15	.14	do	11.2	[7] 12.0		12.7	[7] 13.5	[7] 13.9	14.3	[7] 14.6				Do.[1]
S551	1.17	.35	do	11.0	[7] 11.8		12.9	[7] 13.6	[7] 14.1	14.5	[7] 14.7				Do.[1]
257	1.20	.40	Quenched and drawn	11.6	[7] 12.4										Hidnert.[6]
5 [8]	3.12	2.66	Cast	10.2	10.6		11.6	12.4	13.2	13.7	14.0				Baraduc-Muller.[9]
			Quenched	9.5	9.1		10.7	13.4							
	6	(2)	Cast			[3] 11.3									Ruf.[4]
6 [10]	7.40	1.62	do	10.9	10.7		11.2	12.1	12.9	13.8	15.7	14.7	15.0		Baraduc-Muller.[9]
			Quenched	9.4	9.9		10.5	10.8	11.3	11.6	12.1	12.9	14.5	16.8	
1,218	11.9	.09	Annealed	10.6	10.6		11.0	11.4	11.7						Hidnert and Sweeney.[11]
	12	(2)	Cast			[3] 10.7									Ruf.[4]
1,195	12.0	.09	Annealed		10.2			11.2		12.0					Hidnert and Sweeney.[11]
1,218A	12.2	.09	do	9.8	10.4		10.8	11.2	11.6	11.9		12.3			Do.[11]
1,219	12.2	.09	do	10.2	10.4		10.8	11.2	11.7						Do.[11]
1,219A	12.4	.09	do	9.5	10.3		10.7	11.2	11.6	12.1					Do.[11]
	13	.3	Wrought		10.9										(12).
S565	13.00	.30–.40	Annealed	10.0	[7] 10.4		11.0	[7] 11.4	[7] 11.8	12.2	[7] 12.4				Sonder and Hidnert.[1]
S620	13.10	.30	do	10.3	10.7		[7] 11.3	[7] 11.5	[7] 11.8	12.1	[7] 12.4	[7] 12.5			Do.[13]
S680 [14]	13.10	.30	Hardened	9.6											Do.[13]
				9.9	9.8			[7] 9.8	[7] 10.6	11.2		[7] 11.8			
1,117 [15]	13.5	.13	Annealed		10.4			11.3		12.1		12.8			Hidnert and Sweeney.[11]
				10.2	10.5		10.9	11.3	11.7	12.1		12.6			
1,156 [15]	15.9	.12	do					10.7		11.2					Do.[11]
1,157	16.4	.13	Quenched and drawn				10.8			11.8					Do.[11]

1,156 [15]	15.9	.12	do												
1,157	16.4	.13	Quenched and drawn				10.8	10.7		11.2					Do.[11]
							11.7			11.8					
1,157A	16.4	.13	do	9.9	10.1		10.4	10.9	11.3	11.6		12.4			Do.[11]
1,299	17.04	.04	Hot-rolled	10.6	10.8		11.1	11.4	11.7	11.9	12.1	12.5	13.1		Hidnert.[16]
1,300	17.08	.06	Annealed	10.3	10.7		11.0	11.2	11.4	11.7	11.9	12.4	12.9		Do.[16]
1,300A	17.08	.06	do	10.3	10.5		10.9	11.1	11.3	11.5	11.8	12.3	12.9		Do.[16]
1,427	17.6	.04	do	10.1	10.4		10.7	11.1		11.6	11.8	12.2	12.8		Do.[16]
	18	(2)	Cast			[3] 10.3									Ruf.[4]
	20		Wrought and cast									[17] 11.9			(12).
2,846F [5]	20	<.1	Cast	10.7										12.3	Dean.[6]
	20	.3	Wrought			[18] 9.9			[19] 10.2		[19] 10.3				(18).
1,428	24.6	.74	Annealed	10.2	10.5		10.7	11.0		11.4	11.6	12.0	12.5		Hidnert.[16]
1,294	24.63	.16	Hot-rolled	10.0	10.3		10.6	10.9	11.2	11.3	11.6	12.2	12.7		Do.[16]
	25	(2)	Cast			[3] 10.0									Ruf.[4]
	25		do									[17] 15.3			(12).
CN21-7	26.5	.38	Normalized		10.3			11.0		11.4					Hidnert and Sweeney.[20]
CN21-7	26.5	.38	Quenched		11.7			12.4		12.2					Do.[20]
	32	(2)	Cast			[3] 9.7									Ruf.[4]
2850F [5]	40	<.1	do	9.8										13.7	Dean.[6]
3 [21]	45.9	6.67	do	7.5	7.7		7.7	8.4	8.7	9.1	9.5	9.8	10.0	10.2	Baraduc-Muller.[9]
			Quenched	9.3	8.5		8.6	8.9	9.0	9.2	9.4	9.5	9.5	9.4	
2 [21]	47.60	2.84	Cast	8.0	8.3		8.3	8.8	9.3	9.8	10.2	10.6	10.8	10.9	Do.[9]
			Quenched	9.2	8.9		9.0	9.2	9.8	10.0	10.5	10.8	10.8	10.9	
	50	(2)	Cast			[3] 9.3									Ruf.[4]
4 [21]	53.3	6.21	do	7.5	7.0		7.1	7.4	7.8	8.3	8.7	9.0	9.2	9.3	Baraduc-Muller.[9]
			Quenched	7.2	6.7		6.8	7.2	7.6	7.9	7.9	8.2	8.3	8.4	
2851F [5]	60	<.1	Cast	9.0										13.9	Dean.[6]

[1] B. S. Sci. Paper No. 433; 1922.
[2] Carbon-free.
[3] Obtained from Ruf's curve.
[4] Zeitschrift für Elektrochemie, vol. 34, p. 813; 1928.
[5] All coefficients of expansion except those for the range from room temperature to 100° C. were computed in 1931 from the published data of the observer.
[6] Rensselaer Polytechnic Institute, Engineering and Science Series, No. 26; 1930.
[7] Derived in 1931 from unpublished original data of observers.
[8] Data reported by Mathews, Transactions of the American Institute of Mining and Metallurgical Engineers, vol. 67, p. 133; 1922.
[9] Revue de Métallurgie, vol. 7, p. 657; 1910.
[10] All coefficients of expansion except those for the ranges from room temperature to 100° C. and from room temperature to 900° C. were derived in 1931 from the published data of the observer.
[11] B. S. Sci. Paper No. 570; 1928.
[12] Data furnished by manufacturer of alloy (Proceedings American Society for Testing Materials, vol. 24, p. 189; 1924).
[13] B. S. Sci. Paper No. 426; 1921.
[14] All coefficients of expansion were obtained on second heating except 9.6×10^{-6} (obtained on first heating).
[15] Coefficients on first line were obtained on first heating and those on second line were obtained on second heating.
[16] Present investigation.
[17] From 0° to 800° C.
[18] From 23° to 250 ° C.
[19] Computed from coefficients given in publication cited in footnote 12.
[20] Data reported by Mathews, Transactions of the American Institute of Mining and Metallurgical Engineers, vol. 71, p. 568; 1925.
[21] All coefficients of expansion except those for the ranges from room temperature to 100° C. and from room temperature to 1,000° C. were derived in 1931 from the published data of the observer.

Figure 11 indicates the effects of chromium content, carbon content, heat treatment, etc., on the coefficients of expansion of iron-chromium alloys for various temperature ranges. The data were taken from Table 6. The results plotted in the figure indicate the observers, the ranges of carbon contents of the alloys and their heat treatments. All coefficients of expansion represent values for annealed [8] alloys except those indicated otherwise. The curves of the coefficients of expansion of annealed iron-chromium alloys are summarized in Figure 12 and indicate that the coefficients of expansion increase with temperature and generally decrease with increase in chromium content. For alloys containing from about 12 to 25 per cent chromium, the changes in the coefficients of expansion are small.

3. NICKEL-CHROMIUM-IRON ALLOYS

This subsection gives the results obtained on 26 samples of nickel-chromium-iron alloys containing from 1.3 to 70.1 per cent nickel, 4.9 to 26.7 per cent chromium and 6.6 to 74.7 per cent iron. The chemical composition, heat treatment and other information about the samples have been given in Table 1.

The expansion observations [9] obtained on the nickel-chromium-iron alloys are shown in subsequent figures. Some of the expansion curves show critical regions. A consideration of the nature of nickel-chromium-iron alloys may furnish information relating to the causes of these critical regions.

Bain and Griffiths [10] state "Obviously, no two metals could develop a single homogeneous series of solid solutions unless they were of the same identical type. Thus we can conceive of a continuous series of solid-solution alloys from pure alpha (or delta) iron to pure chromium or from pure gamma iron to pure nickel, and this is precisely what exists. Hence, first of all the ternary diagram is certain to contain two solid solutions—one embracing gamma iron and nickel with some chromium in solution and the other embracing alpha (or delta) iron and chromium and containing some nickel. There will be the two-phase zone between these single solutions types."

Pomey and Voulet [11] published a ternary diagram [12] of nickel-chromium-iron alloys in conjunction with the equilibrium diagrams of nickel-chromium, iron-chromium, and iron-nickel alloys. Figure 13 shows the ternary diagram and the equilibrium diagrams mentioned. (The ternary diagram has been reproduced on an enlarged scale.) Pomey and Voulet divided the ternary diagram representing the nickel-chromium-iron system into nine regions as follows:

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[8] The curves indicated in the figure were obtained from the coefficients of expansion of annealed alloys investigated at the National Bureau of Standards by Souder, Hidnert, and Sweeney between 1921 and 1931, inclusive. The dotted portions of the curves indicate that sufficient data have not been obtained in the region of low chromium content.

[9] Portions of some expansion curves are indicated by dotted lines in order to show that sufficient observations have not been obtained. Some duplicate samples (marked A) were investigated in order to obtain additional data.

[10] E. C. Bain and W. E. Griffiths, Transactions American Institute of Mining and Metallurgical Engineers, vol. 75, p. 166; 1927.

[11] J. Pomey and P. Voulet, Chimie & Industrie (special number), February, 1929, p. 404.

[12] After the present manuscript was completed, the author's attention was called to a recent preliminary ternary diagram by R. H. Aborn and E. C. Bain (Transactions American Society for Steel Treating, vol. 18, p. 837; 1930). They state that the greatest usefulness of the ternary diagram is in indicating the trends which may be expected in individual compositions, and for this purpose the highest accuracy is not required. The construction of the ternary system, in accordance with the phase rule and the binary systems, was also recently derived by F. Wever and W. Jellinghaus (Mitt. Kaiser-Wilhelm-Inst. Eisenforsch. Düsseldorf, vol. 12, p. 93; 1931) and the boundaries of the space sections were determined approximately by thermic, dilatometric, metallographic and X-ray investigations.

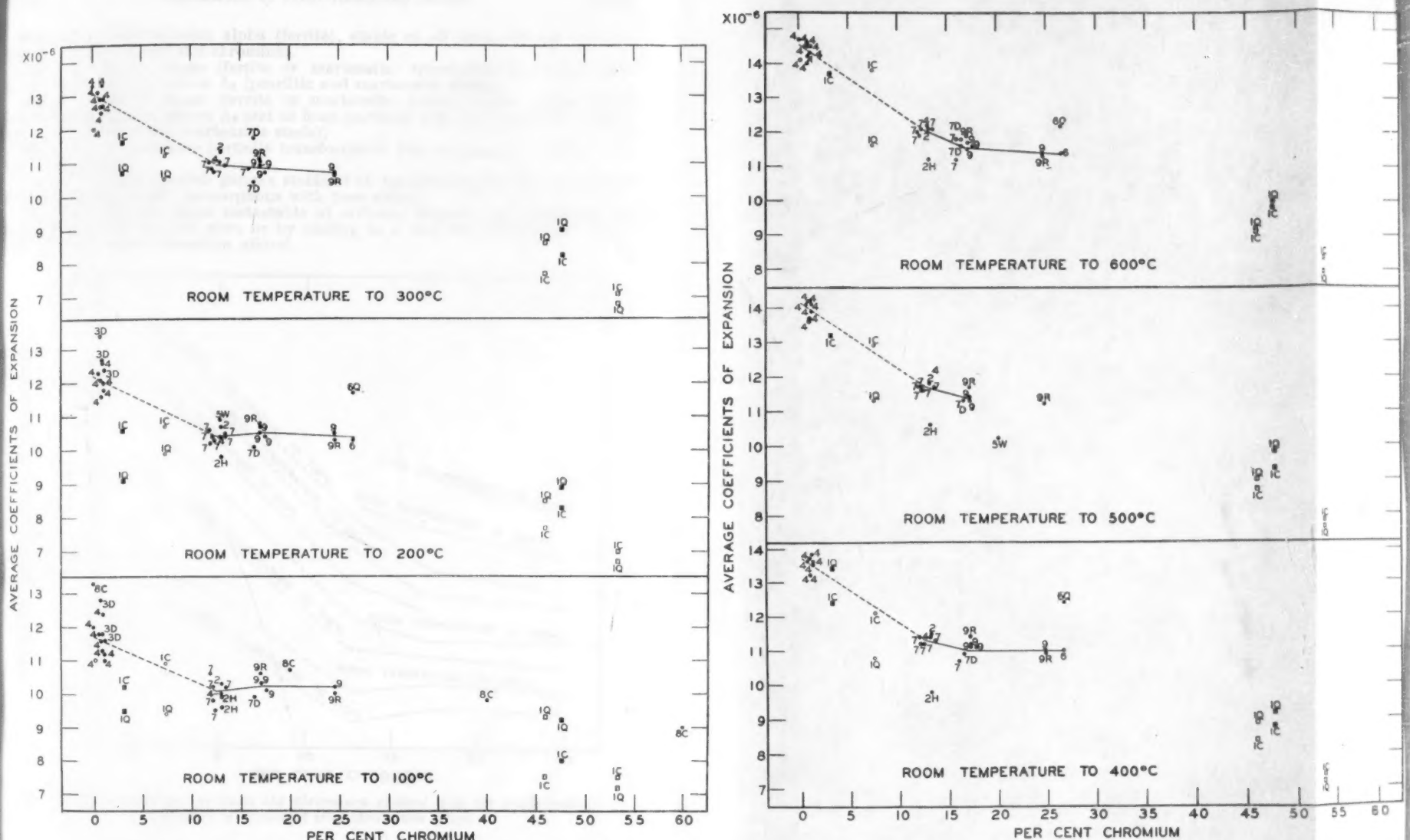


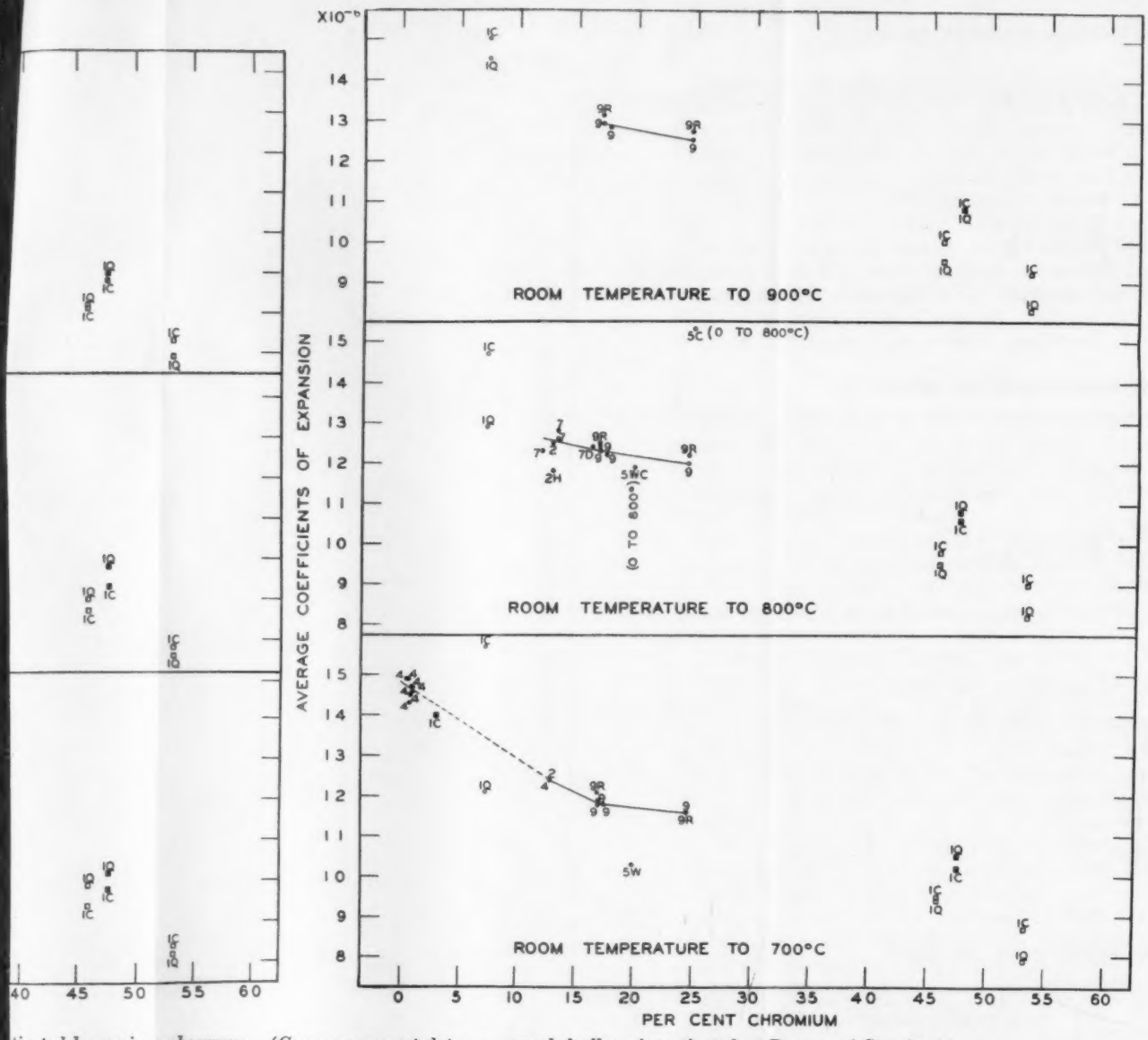
FIGURE 11.—*Effects of chromium content, carbon content, and heat treatment on the coefficients of expansion of iron-chromium alloys investigated by various observers.* (C

The following symbols were used:

Observer	Date
1. Baraduc-Muller	1910
2. Souder and Hidnert	1921
3. Hidnert	1922
4. Souder and Hidnert	1922
5. ?	1924
6. Hidnert and Sweeney	1925
7. Hidnert and Sweeney	1928
8. Dean	1930
9. Hidnert	1931

C=Cast.
D=Quenched and drawn.
H=Hardened.
Q=Quenched.
R=Hot-rolled.
W=Wrought.

NOTE.—Every point not marked with a letter represents an annealed alloy.
●=0 to 1 per cent carbon.
○=1 to 2 per cent carbon.
■=2 to 3 per cent carbon.
□=6 to 7 per cent carbon.



tigated by various observers. (*Curves represent data on annealed alloys investigated at Bureau of Standards*)

Date
1910
1921
1922
1922
1924
1925
1928
1930
1931

alloy.

Region 1.—Solid solution alpha (ferrite), stable at all temperatures, isomorphous with alpha iron and chromium.

Region 2.—Alpha phase (ferrite or martensite) transformable entirely into austenite by heating above A_3 (pearlitic and martensitic steels).

Region 3.—Alpha phase (ferrite or martensite) transformable entirely into austenite by heating above A_3 and at least partially into delta iron by heating above A_4 (pearlitic and martensitic steels).

Region 4.—Alpha phase partially transformable into austenite by heating to a high temperature.

Region 5.—Solid solution gamma stable at all temperatures (reversible nickel-iron-chromium alloys), isomorphous with pure nickel.

Region 6.—Gamma phase metastable at ordinary temperature, transformable into alpha phase by cold work or by cooling to a very low temperature (irreversible iron-nickel-chromium alloys).

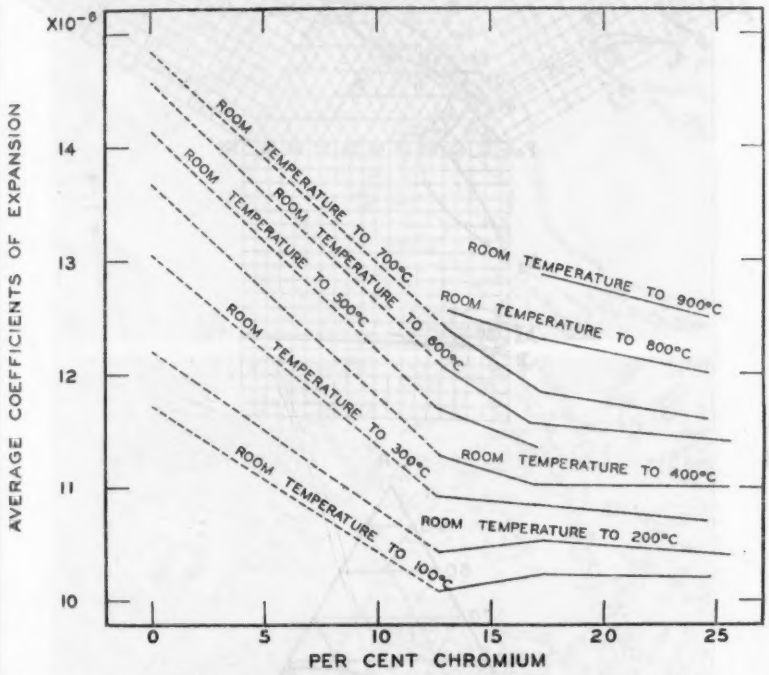


FIGURE 12.—*Relations between the chromium content and the coefficients of expansion of annealed iron-chromium alloys*

Region 7.—Gamma phase metastable like the preceding, but in addition to this can be transformed into delta phase by heating to a very high temperature.

Region 8.—Mixture of metastable alpha and gamma phases, the proportion varying with the temperature of the tempering.

Region 9.—Mixture of two phases 1 and 5, respectively, isomorphous with chromium and nickel.

The nickel-chromium-iron alloys used in the present investigation may be classified in accordance with the regions indicated in the ternary diagram which is based on binary diagrams of the nickel-chromium, iron-chromium, and nickel-iron systems containing little or no carbon. The regions in which the alloys have been placed, will be indicated in the following paragraphs.

Region 1.—Figure 14 shows expansion data on two samples (1,314 and 1,314A) of cast nickel-chromium-iron alloy (Ni 1.3, Cr 26.7,

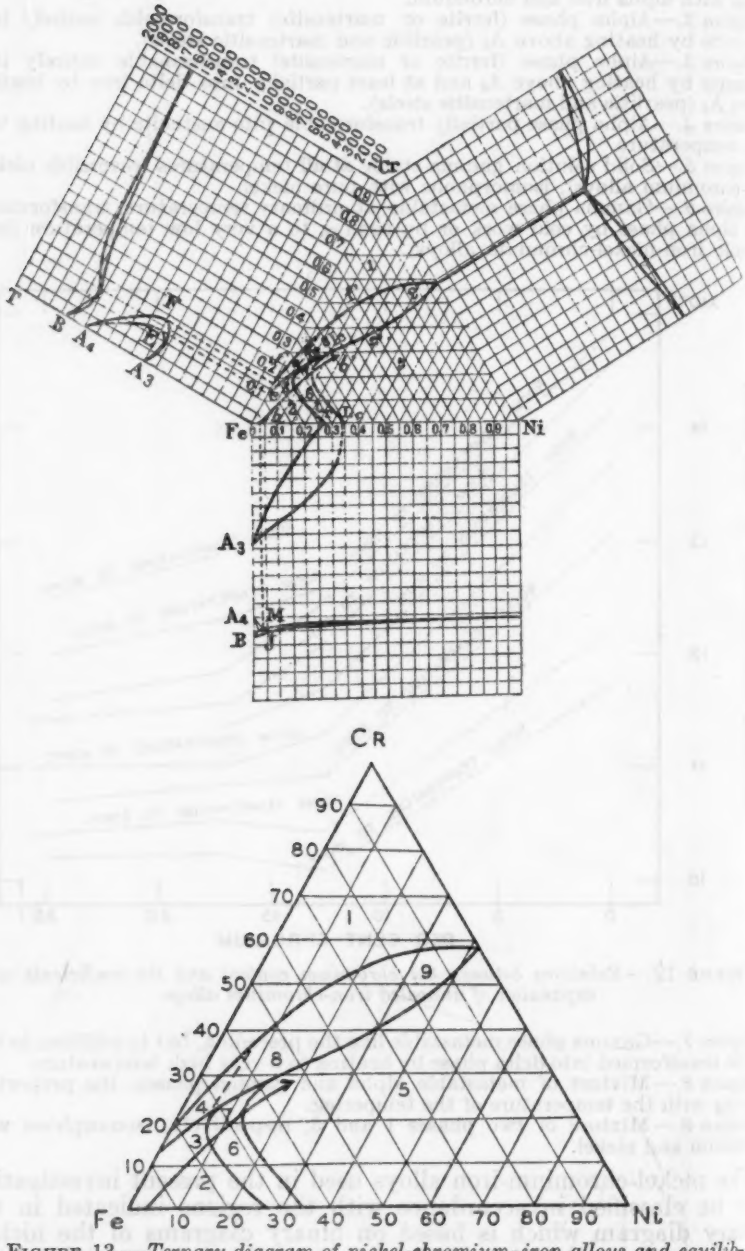


FIGURE 13.—*Ternary diagram of nickel-chromium-iron alloys and equilibrium diagrams of nickel-chromium, iron-chromium, and iron-nickel alloys (Pomey and Voulet)*

An enlarged view of the ternary diagram is shown in the lower part of the figure.

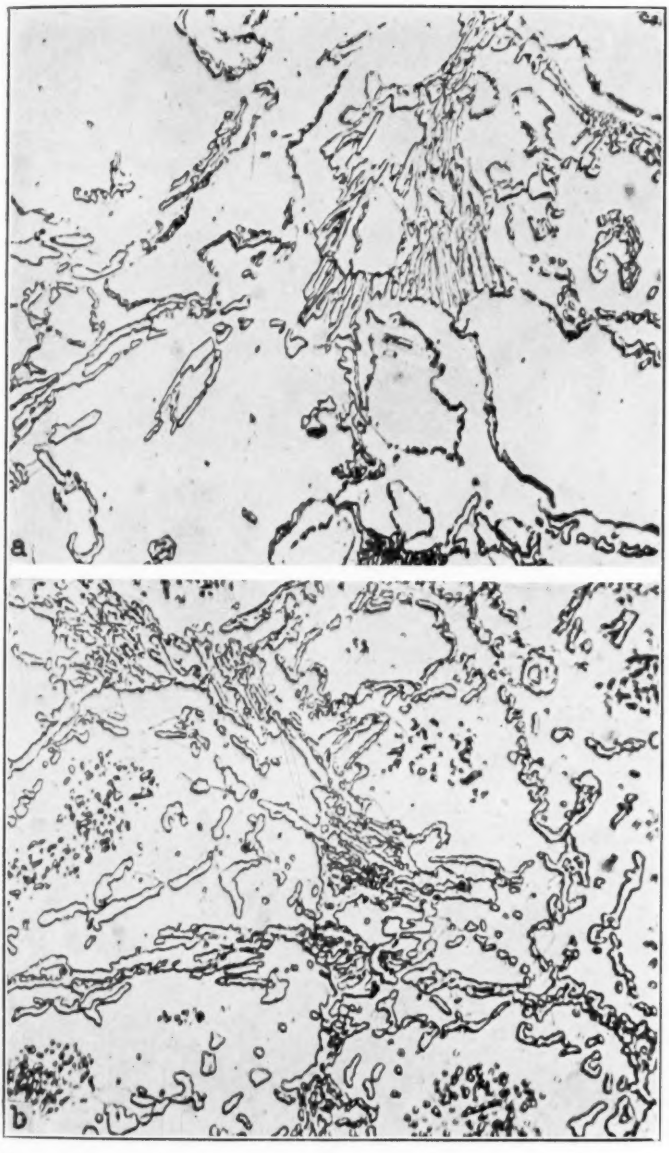


FIGURE 15.—*Microstructure of nickel-chromium-iron alloy (1314A).* × *500*

Ni 1.3, Cr 26.7, Fe 70.0, C 0.72, Mn 0.57, Si 0.66 per cent. *a*, As cast; *b*, after second expansion test.

C 0.72 per cent). The expansion curve for the first heating on each sample shows a rapid increase in expansion between 700° and 800° C.

Figure 15 shows two micrographs [13] of sample 1314A as cast and after the second expansion test. These micrographs indicate that the heat treatment incident to the expansion determinations caused a precipitation of carbide particles from the solid solution alpha (ferrite). It appears that the precipitation of carbide caused the rapid increase in expansion [14] between 700° and 800° C.

In the second expansion test of sample 1314A, the expansion curve does not show a rapid increase in expansion. The alloy therefore

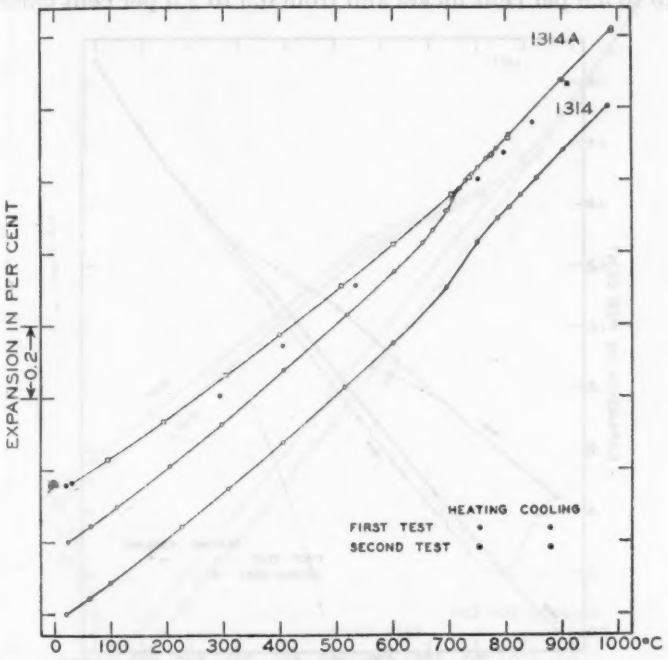


FIGURE 14.—*Linear thermal expansion of two samples of cast nickel-chromium-iron alloy*

Ni 1.3, Cr 26.7, Fe 70.0, C 0.72, Mn 0.57, Si 0.66 per cent.

appears to be stable (between 20° and 1,000° C.) after the precipitation of carbide in the first expansion test.

Region 3.—Figures 16 and 17 show the expansion observations obtained on two samples (1411 and 1411A) of hot-rolled nickel-chromium-iron alloy (Ni 7.5, Cr 14.0, C 0.30 per cent) containing appreciable amounts of silicon and tungsten. The expansion curve on the first heating in each hot-rolled sample (austenitic) does not indicate a transformation, but on cooling from about 200° C. to room tempera-

[13] Microscopic examination of sample 1314A and other samples in this paper was made by E. C. Groesbeck and H. O. Willier, of the National Bureau of Standards. Small pieces for microscopic examination were cut transversely from the rods used in the thermal expansion investigation. The etching reagent was a mixture of 2 parts concentrated hydrochloric acid, 1 part concentrated nitric acid, and 3 parts glycerine (by volume). The magnification for all the micrographs was 500 diameters.

[14] It is possible to classify samples 1314 and 1314A in region 4, for they are near the border between regions 1 and 4. The rapid increase in expansion between 700° and 800° C. may then be assumed to be due to the partial transformation from one phase to another.

ture there is a marked expansion due to a transformation from austenite to the alpha phase (ferrite or martensite). In the second heating above 600° C. there is a transformation from the alpha phase to austenite. In the second cooling (1411A) the curve nearly coincides with the curve obtained in the first cooling, and also indicates the transformation from austenite to alpha phase. The expansion curve on the third heating (1411A) is similar to the curve on the second heating.

Two nickel-chromium-iron alloys investigated by Andrew, Rippon, Miller, and Wragg [15] and two alloys by Souder and Hidnert [16] contain from 0.5 to 3.9 per cent nickel and from 0.5 to 2.5 per cent chromium.

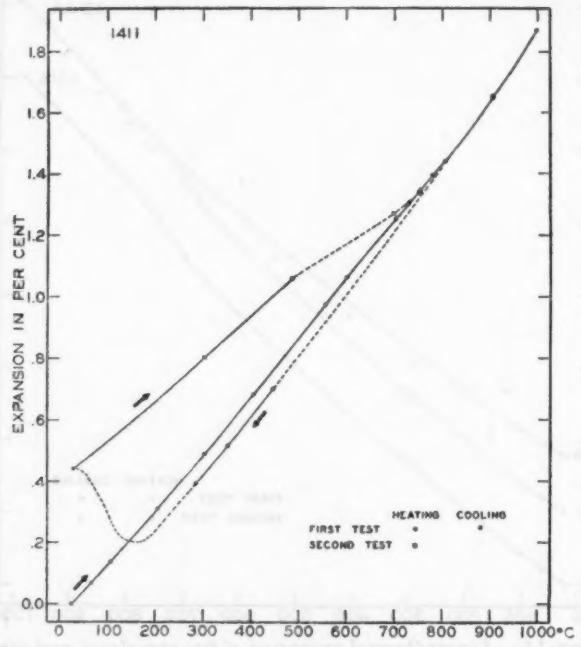


FIGURE 16.—*Linear thermal expansion of hot-rolled nickel-chromium-iron alloy*

Ni 7.5, Cr 14.0, Fe 74.7, C 0.30, Mn 0.17, Si 2.40, P 0.014, S 0.012, W 0.89 per cent.

These alloys may also be classified in region 3. The expansion curves indicate transformations in these alloys.

Region 5.—All of the cast nickel-chromium-iron alloys investigated, except samples 1314, 1314A, 1296, 1296A, and 1303, may be placed in region 5 of the ternary diagram. (Fig. 13.) The alloys in this region form solid solutions of gamma iron and chromium in nickel. Bain and Griffiths [17] state that these compositions are without transformation and that a very long annealing treatment causes some precipitation of excess carbide in parallel planes within the grains.

[15] J. H. Andrew, J. E. Rippon, C. P. Miller, and A. Wragg, Journal Iron and Steel Institute, vol. 101, p. 527; 1920.
[16] W. Souder and P. Hidnert, B. S. Sci. Paper No. 433; 1922.
[17] See footnote 10, p. 1044.

Figures 18 to 23, inclusive, show the expansion data obtained on the 10 cast nickel-chromium-iron samples (1306, 1306A, 1295, 1304, 1291, 1302, 1298, 1305, 1301, and 1313) grouped in region 5. Nearly all of the samples contain appreciable amounts of manganese and silicon. The expansion curve for the first heating (to about 1,000° C.) on each sample except samples 1298 [18] and 1313,[19] shows a retardation or decrease in expansion between 700° and 800° C. The contraction

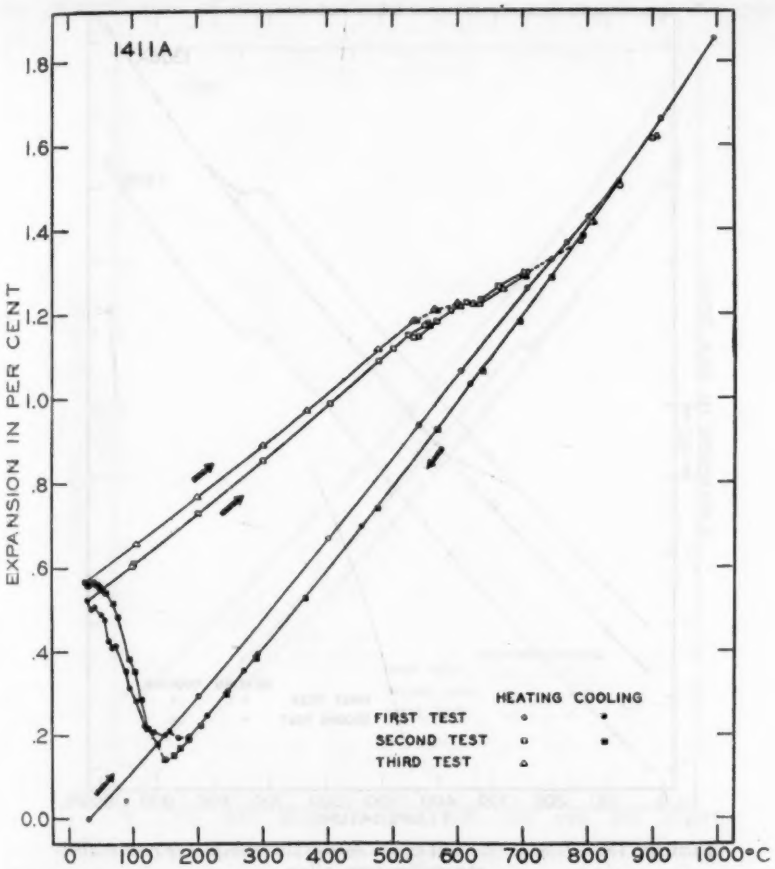


FIGURE 17.—*Linear thermal expansion of hot-rolled nickel-chromium-iron alloy*

Ni 7.5, Cr 14.0, Fe 74.7, C 0.30, Mn 0.17, Si 2.40, P 0.014, S 0.012, W 0.89 per cent.

or retardation in expansion generally appears to decrease with increase in nickel content. The curves on cooling do not show critical regions.

Figures 24 to 27, inclusive, show micrographs obtained on four of the cast alloys (1295, 1302, 1298, and 1313) before and after expansion tests. These micrographs indicate that the heating during the expansion tests caused precipitation of excess carbide from solid solution gamma (austenite). The appreciable contraction on heating, with a

[18] Before observation 11 (fig. 22) sample was heated to about 800° C. when heating current was broken for one and one-fourth hours; sample cooled to about 600° C. (observation 11).

[19] Contains largest contents of manganese and silicon.

resultant decrease in expansion, noted for samples 1295 and 1302 appears to be connected with the precipitation of the carbide particles.

The expansion curves obtained on the second or third heating (to 1,000° C.) of the cast alloys do not show retardation or decrease in expansion. The curves on heating and cooling are nearly reversible between room temperature and 1,000° C. The alloys therefore appear to be stable after the precipitation of excess carbide in the

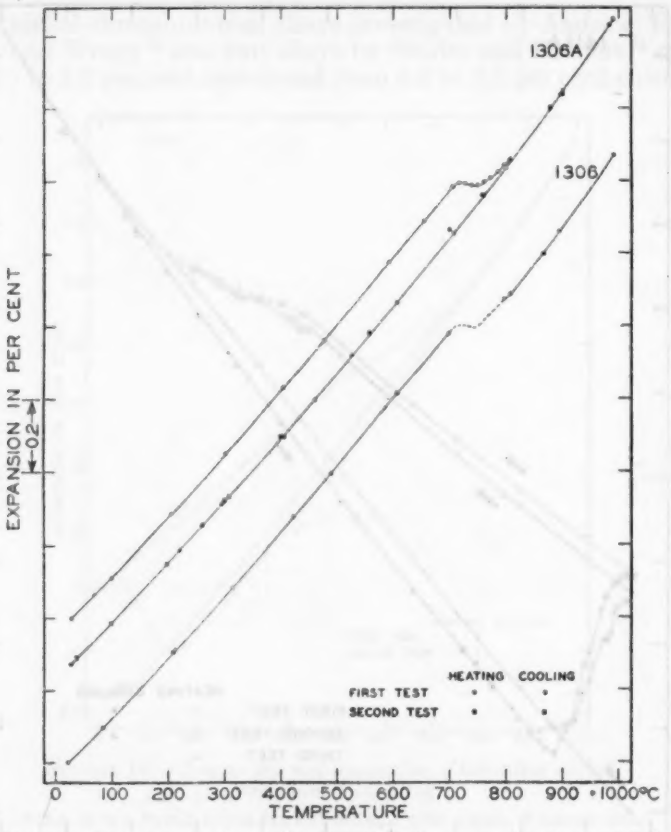


FIGURE 18.—*Linear thermal expansion of two samples of cast nickel-chromium-iron alloy*

Ni 19.55, Cr 19.55, Fe 58.93, C 1.25, Mn 0.15, Si 0.09, Cu 0.48 per cent.

first heating. The precipitation of carbide was probably complete during the first heating.

Before the third expansion tests were made on samples 1295 and 1302 (figs. 19 and 21), they were heated from room temperature to 900° C. in hydrogen and cooled to room temperature in hydrogen. No effect due to hydrogen[20] was observed on the expansion curves obtained in the third tests.

[20] H. S. Rawdon, P. Hidnert, and W. A. Tucker, Transactions American Society for Steel Treating, vol. 10, p. 233; 1926.

Figure 28 shows reversible expansion curves of two hot-rolled alloys (1404 and 1403) that are austenitic and stable (between room temperature and 1,000° C.).

Region 6.[21]—Figure 29 shows the expansion data obtained on a cast alloy (1303). The curve obtained on heating in the second [22] expansion test shows a retardation in expansion between 700° and 800° C. This retardation in expansion was apparently caused by the precipitation of excess carbide which is indicated by the micro-

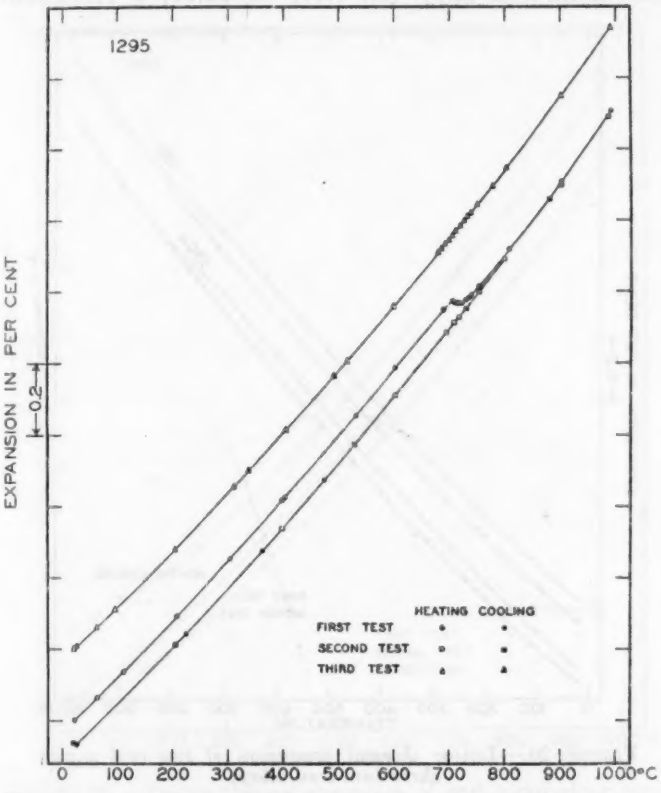


FIGURE 19.—*Linear thermal expansion of cast nickel-chromium-iron alloy*

Ni 27.78, Cr 18.50, Fe 50.30, C 0.58, Mn 0.83, Si 1.90, Al 0.08 per cent.

graphs [23] in Figure 30. The carbide was precipitated from the solid solution gamma (austenite), as was found in cast alloys of region 5.

The curves obtained in the third and fourth [24] expansion tests on sample 1303 do not show retardations in expansion. After the precipitation of carbide in the second expansion test the sample appeared to be stable between 20° and 1,000° C.

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[21] Data on a loys near the border between regions 6 and 7 will be discussed later.

[22] First test only to about 300° C.

[23] It is interesting to note that the micrograph of the heat-treated sample shows that the carbide particles are concentrated along the network of the dendritic structure.

[24] Before the fourth expansion test, the sample was heated and cooled in hydrogen, in a similar manner as was done with samples 1295 and 1302 (region 5).

Figure 31 shows the expansion curve of a forged and annealed austenitic nickel-chromium-iron alloy (1310). This curve does not indicate any transformation between room temperature and 1,000° C.

Data on the thermal expansion of similar alloys at low temperatures are necessary in order to confirm Pomey and Voulet's statement relating to the transformation from gamma phase to alpha phase.

Region 7.[25]—Figures 32 to 34, inclusive, show the results obtained on the thermal expansion of two cast samples (1296 and 1296A) of nickel-chromium-iron alloy (Ni 8.41, Cr 21.66, C 1.15) containing

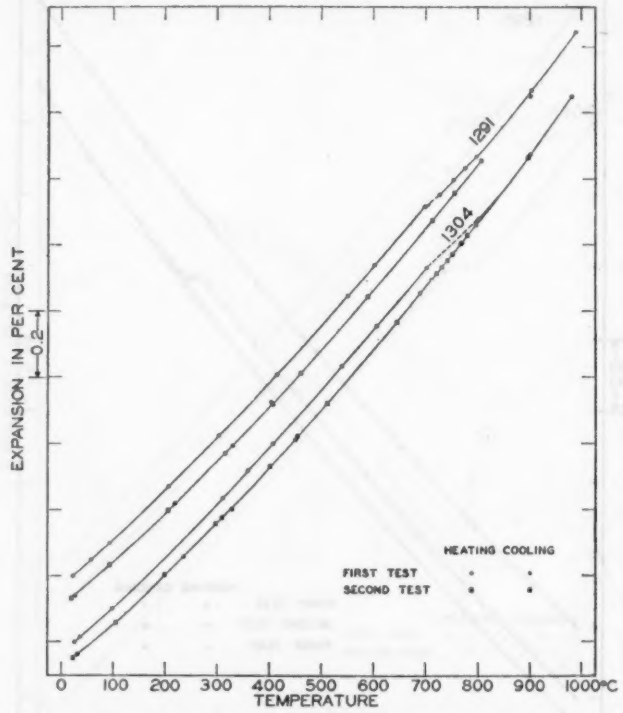

FIGURE 20.—*Linear thermal expansion of two cast nickel-chromium-iron alloys*

1304, Ni 36.0, Cr 16.4, Fe 45.4, C 0.42, Mn 0.71, Si 1.03 per cent.
1291, Ni 40.3, Cr 21.1, Fe 34.6, C 0.44, Mn 1.43, Si 1.91, Al<0.1, Cu 0.1 per cent.

appreciable amounts of manganese, silicon, and aluminum. The samples during the first heating were in the gamma phase, and the retardation in expansion between 700° and 800° C. was apparently due to the precipitation of excess carbide. The curves on cooling from 1,000° C. to room temperature (first test) show marked expansion from about 100° C. to room temperature, due to a transformation from the gamma phase to the alpha phase.

[25] Data on alloys near the border between regions 6 and 7 will be discussed later.

On reheating sample 1296A to about 700° C. (see second test), the alpha phase changed to the gamma phase. This phase was heated to 1,000° C. and then cooled to about 120° C. At the latter temperature a marked expansion occurred with further cooling to about 50° C., due to a transformation from gamma phase to alpha phase. The alpha phase indicated normal contraction on cooling from 50° C. to room temperature.

Sample 1296A (third test) was then cooled from room temperature to −50° C., heated from −50° to +250° C., and finally cooled to

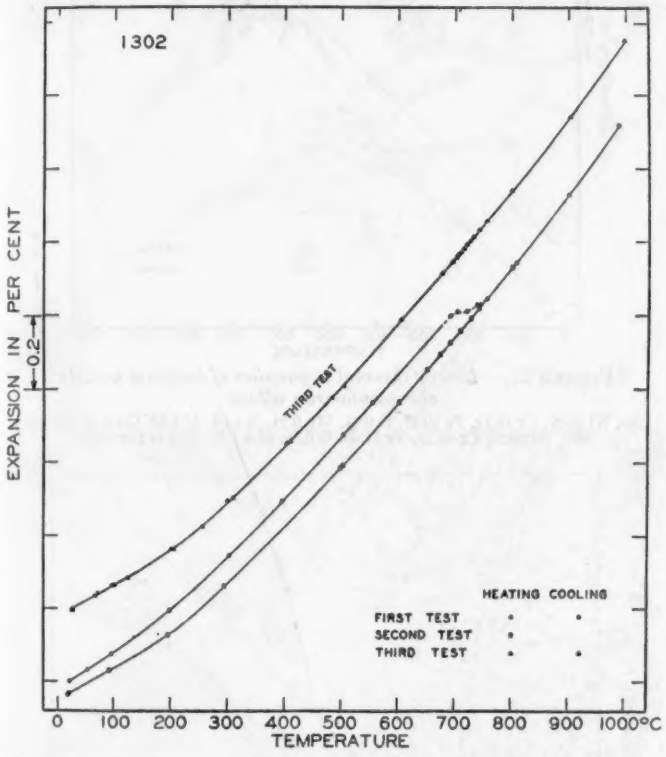

FIGURE 21.—*Linear thermal expansion of cast nickel-chromium-iron alloy*

Ni 41.98, Cr 12.12, Fe 44.10, C 0.43, Mn 0.55, Si 0.81 per cent.

room temperature. The expansion curve does not show a transformation.

The results indicate that the alpha phase for this alloy is stable at low temperatures, and when heated to about 700° C. transforms to the gamma phase. Between room temperature and about 700° C. the alloy may be either in the alpha or gamma phase. Above 700° the alloy is in the gamma phase and, according to Pomey and Voulet, in the delta phase at very high temperatures.

Figure 35 shows the microstructure of sample 1296 as cast and after the second expansion test.

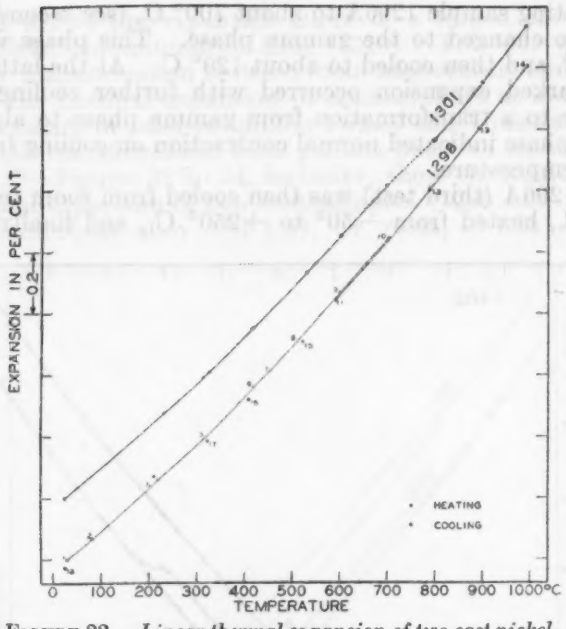

FIGURE 22.—*Linear thermal expansion of two cast nickel-chromium-iron alloys*

1298, Ni 58.07, Cr 19.12, Fe 19.21, C 0.54, Mn 0.94, Si 1.69, Al 0.03, Cu 0.13 per cent.
1301, Ni 65.22, Cr 16.23, Fe 15.33, C 0.59, Mn 1.40, Si 1.18 per cent.

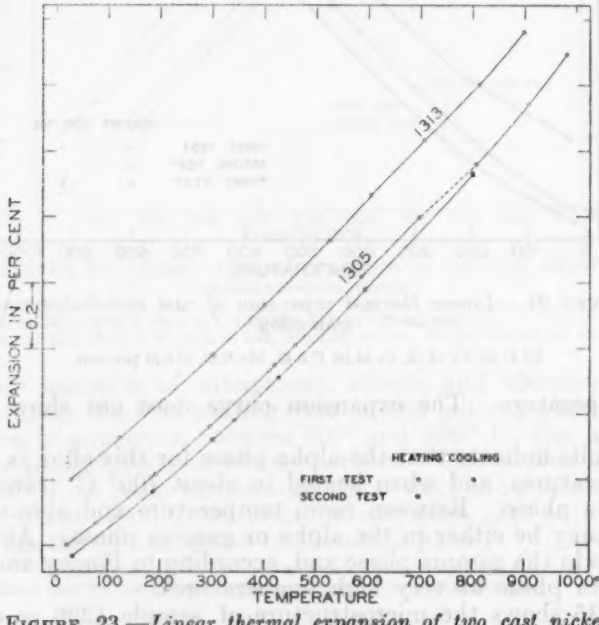

FIGURE 23.—*Linear thermal expansion of two cast nickel-chromium-iron alloys*

1305, Ni 61.00, Cr 15.70, Fe 20.26, C 0.95, Mn 0.62, Si 0.69, Cu 0.78 per cent.
1313, Ni 70.1, Cr 16.3, Fe 6.6, C 0.94, Mn 3.23, Si 2.51, Al<0.1, Cu<0.1 per cent.

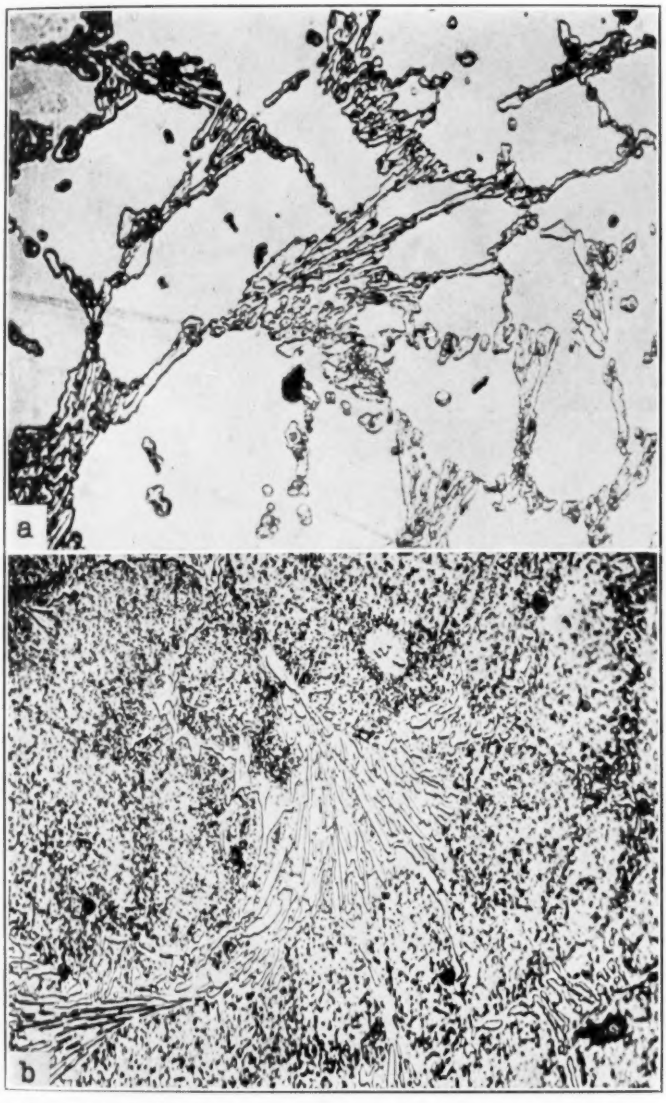

FIGURE 24.—*Microstructure of nickel-chromium-iron alloy (1295).*
× 500

Ni 27.78, Cr 18.50, Fe 50.30, C 0.58, Mn 0.83, Si 1.90, Al 0.08 per cent. *a*, As cast; *b*, after second expansion test.

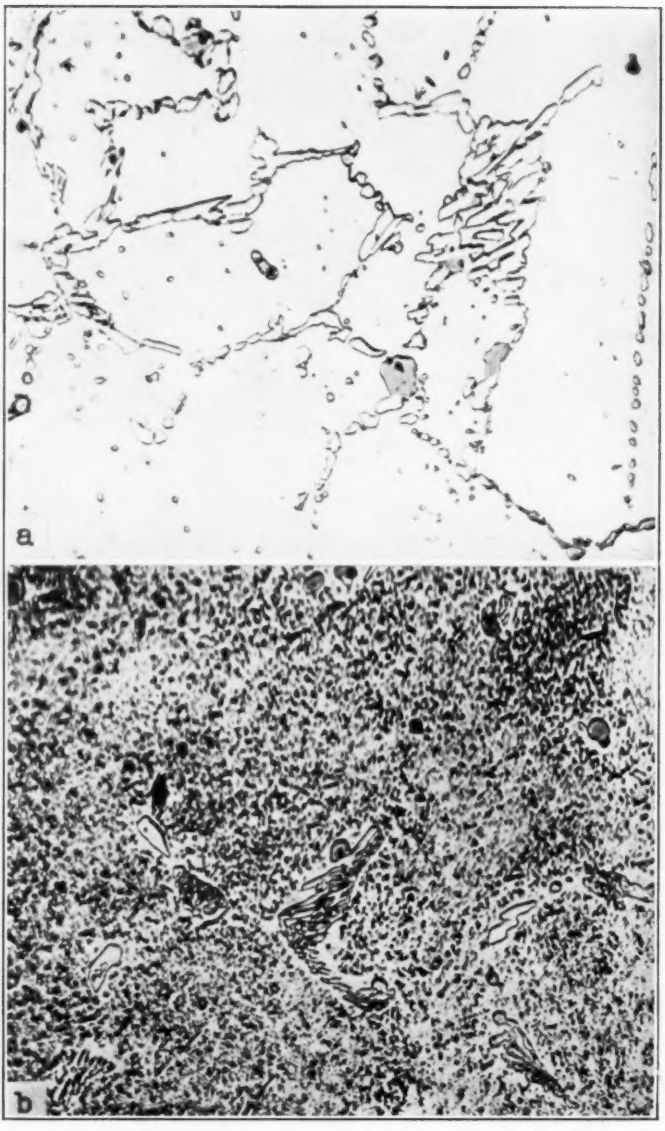

FIGURE 25.—*Microstructure of nickel-chromium-iron alloy (1302).*
× 500

Ni 41.98, Cr 12.12, Fe 44.10, C 0.43, Mn 0.55, Si 0.81 per cent. *a*, As cast; *b*, after second expansion test.

FIGURE 26.—*Microstructure of nickel-chromium-iron alloy (1298).*
× 500

Ni 58.07, Cr 19.12, Fe 19.21, C 0.54, Mn 0.94, Si 1.69, Al 0.03, Cu 0.13 per cent. *a*, As cast; *b*, after expansion test.

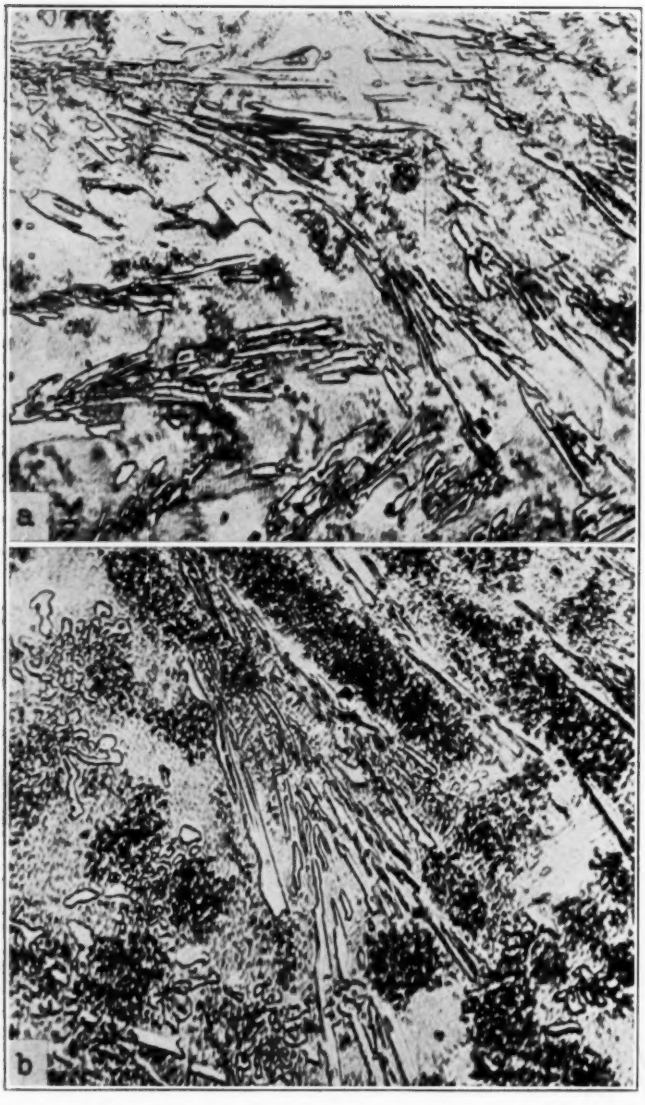

FIGURE 27.—*Microstructure of nickel-chromium-iron alloy (1313).* × *500*

Ni 70.1, Cr 16.3, Fe 6.6, C 0.94, Mn 3.23, Si 2.51, Al<0.1, Cu<0.1 per cent. *a*, As cast; *b*, after expansion test.

Regions 6 and 7.—Alloys 1297, 1418, 1424, 1419, 1311, and 1312 will be grouped together, for they are near the border between regions 6 and 7.

Figure 36 shows the expansion curve of alloy 1297 which was hot-rolled, cooled in brine, annealed and air cooled. This curve indicates retardation in expansion between 700° and 750° C., apparently due to the precipitation of carbide. Figure 37 shows the microstructure of the alloy before and after the expansion test. The relatively small amount of the structurally free constituents (presumably carbide) in the microstructure of this material may be due to the hot working before the expansion test and to the low carbon content.

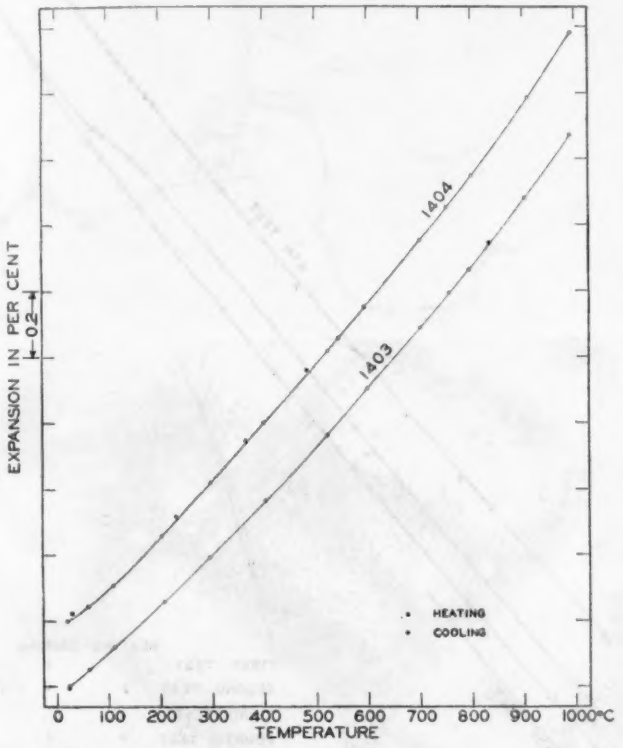

FIGURE 28.—*Linear thermal expansion of two hot-rolled nickel-chromium-iron alloys*

1404, Ni 30.1, Cr 4.9, Fe 63.9, C 0.20, Mn 0.64, Si 0.22, P 0.013 per cent.
1403, Ni 63.0, Cr 15.9, Fe 18.1, C 0.08, Mn 2.14, Si 0.78, P 0.013 per cent.

Figure 38 shows the expansion and contraction curve of sample 1,418 (carbon 0.12 per cent) which was hot rolled and annealed. No critical region was found on heating or cooling between 20° and 1,000° C.

Figure 39 shows the results obtained on the thermal expansion of two quenched alloys (1424 and 1419) containing 0.06 per cent carbon. The expansion curves do not show critical regions.

Figure 40 shows the expansion curves of two alloys (1,311 and 1,312) which were forged and annealed. These curves do not indicate critical

regions. Figure 41 shows the microstructure of sample 1312 after the expansion determinations. The small amount of the structurally-free constituents (presumably carbide) may be due to the hot working before the expansion test and to the low carbon content.

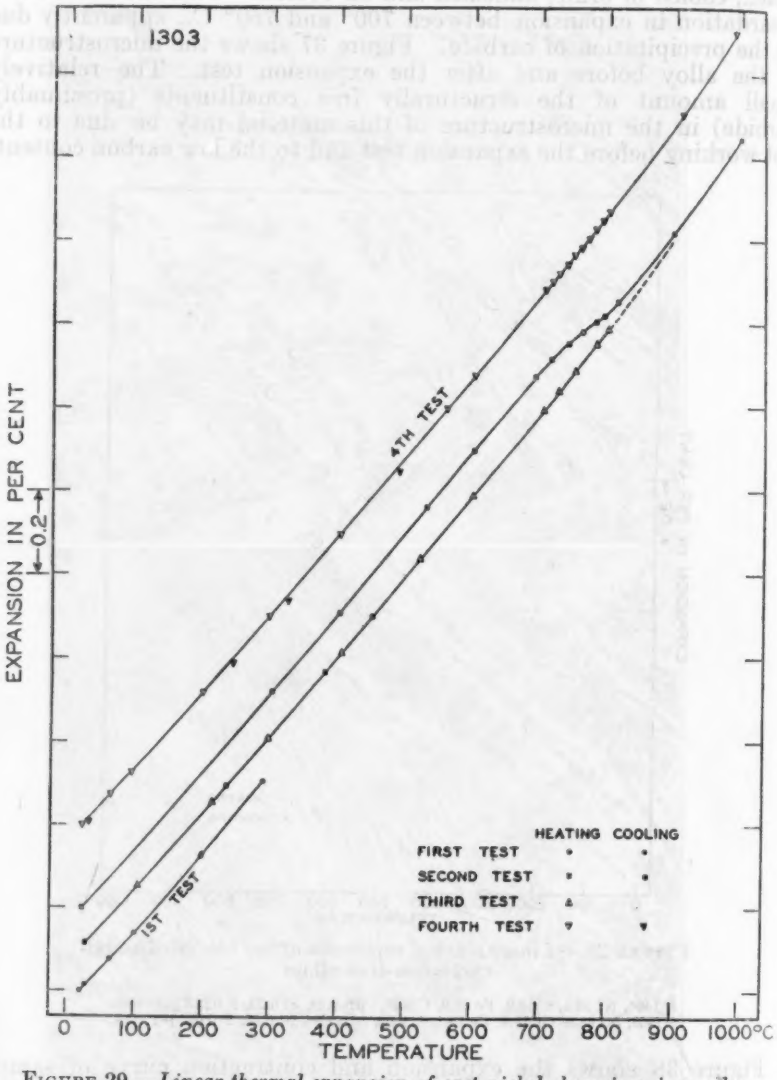

FIGURE 29.—*Linear thermal expansion of cast nickel-chromium-iron alloy*
Ni 19.80, Cr 7.76, Fe 69.30, C 0.49, Mn 0.32, Si 1.03, V 0.46 per cent.

All of these alloys near the border between 6 and 7 appear to be austenitic (gamma phase). The expansion curves between 20° and 1,000° C. do not indicate transformation from this phase to another phase. Data on the thermal expansion of these or similar alloys at low temperatures (below 20° C.) will be necessary in order to determine if there are transformations from the gamma phase to the alpha phase.

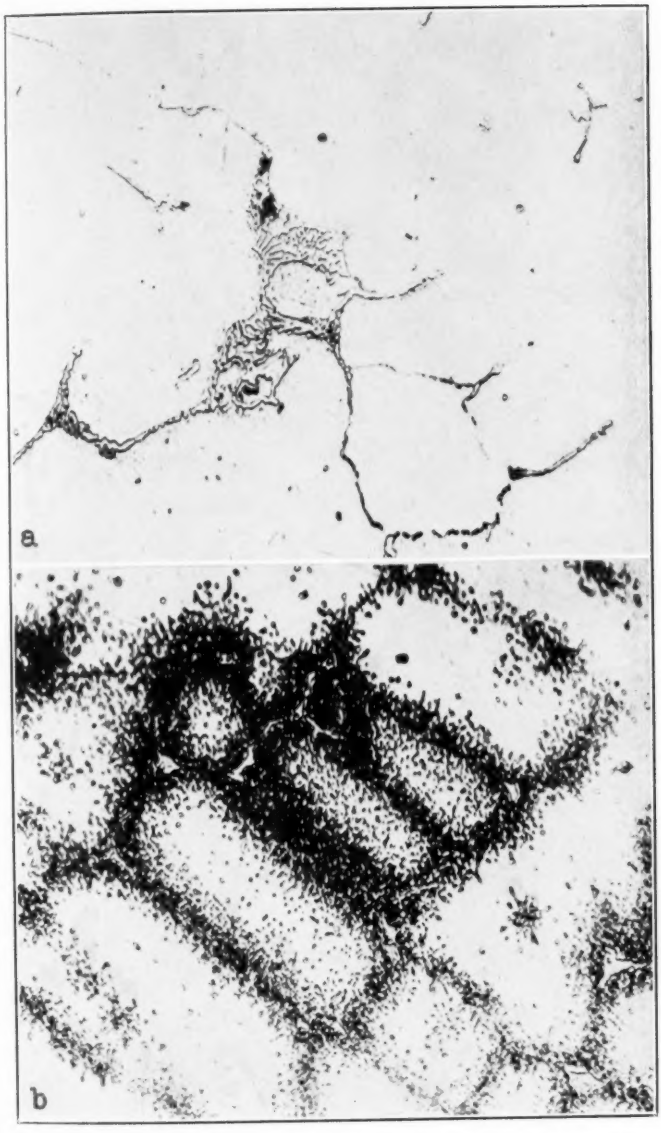

FIGURE 30.—*Microstructure of nickel-chromium-iron alloy (1303).* × *500*

Ni 19.80, Cr 7.76, Fe 69.30, C 0.49, Mn 0.32, Si 1.03, V 0.46 per cent. *a*, As cast; *b*, after second expansion test.

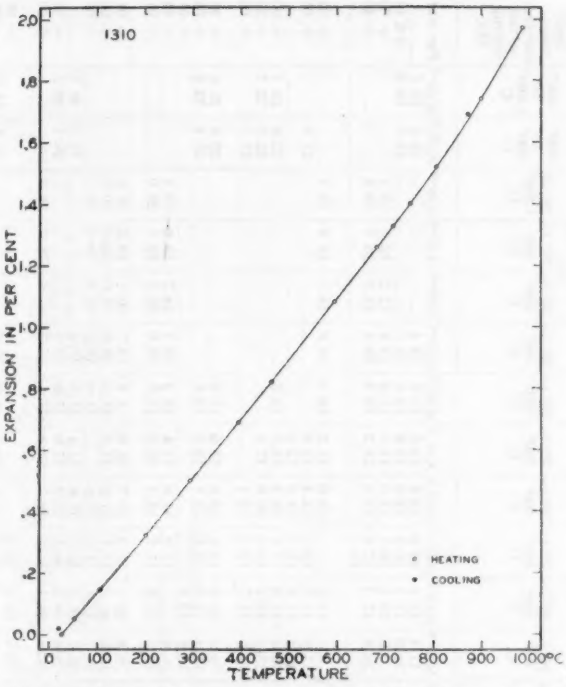

FIGURE 31.—*Linear thermal expansion of forged and annealed nickel-chromium-iron alloy*

Ni 20.2, Cr 7.9, Fe 69.6, C 0.39, Mn 0.74, Si 1.12 per cent.

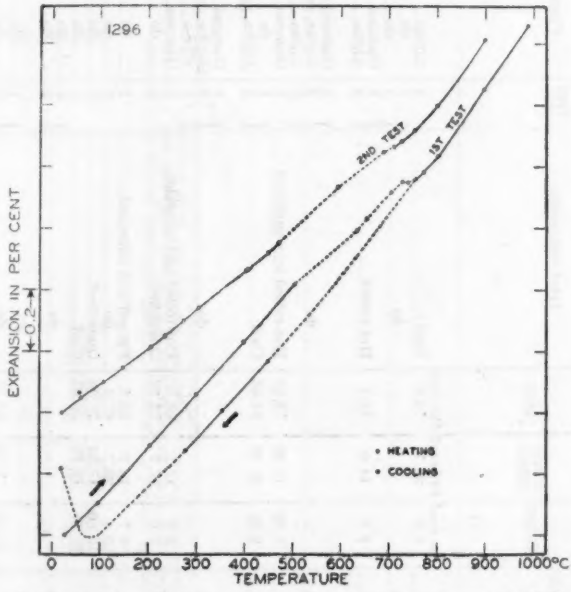

FIGURE 32.—*Linear thermal expansion of cast nickel-chromium-iron alloy*

Ni 41, Cr 21.66, Fe 64.63, C 1.15, Mn 1.16, Si 1.24, Al 1.57, Cu 0.10 per cent.

TABLE 7.—*Average coefficients of expansion of nickel-chromium-iron alloys*

Sample	Chemical composition: Nickel	Chromium	Iron	Heat treatment	Test No.	Phase	Average coefficients of expansion per degree centigrade: 20° to 60° C.	20° to 100° C.	20° to 200° C.	20° to 300° C.	20° to 400° C.	20° to 500° C.	20° to 600° C.	20° to 700° C.	20° to 800° C.	20° to 900° C.	20° to 1,000° C.	800° to 900° C.	800° to 1,600° C.	Change in length due to heat treatment received during test
	Per cent	*Per cent*	*Per cent*				×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	*Per cent*
1314	1.3	26.7	70.0	Cast	1	Alpha	10.7	11.4	11.7	12.0	12.4	12.6	12.9	13.4				16.5	15.7	
1314A				do	1	do	10.6	11.0	11.5	11.9	12.3	12.6	12.8	13.7				16.6	16.2	+0.16
1411	7.5	14.0	74.7	Hot-rolled	2	do		9.8	10.3	10.7	11.0	11.3	11.5	11.8	12.2	12.7	13.1			+.00
					1	Gamma	16.7	16.8	17.2	17.6	17.9	18.2	18.5	18.5	18.5	18.7	19.3			+.43
1411A				do	2	Alpha				13.1										
					1	Gamma			17.3		18.0	18.3	18.5	18.6	18.5	18.8	19.3			
1297	7.80	17.28	73.62	Hot-rolled and annealed	2	Alpha, gamma		11.9	11.9	12.1	12.4	12.6						21.9		+.53
					3	Alpha		11.4	11.6	11.7	11.9	12.2								+.05
1296	8.41	21.66	64.63	Cast	1	Gamma	16.2	16.4	17.0	17.7	18.2	18.6	19.0					22.9	24.3	+.00
					1	do	15.5	15.2	16.3	16.6	16.9	17.1						22.5	22.7	+.23
					2	Alpha, gamma	12.0	11.6	11.7	12.1	12.1							21.6		+.02
1296A				do	1	Gamma	15.4	15.4	16.0	16.5	16.8	17.0	17.3					20.8	21.6	+.25
					2	Alpha, gamma	11.9	11.4	11.8	12.1	12.1	12.2	12.6					21.4	22.2	+.06
1418	8.9	17.5	69.6	Hot-rolled and annealed	3	Alpha	10.8	10.8	10.8											−.01
1424	9.6	17.7	72.0	Quenched	1	Gamma	16.1	16.4		17.2	17.6	17.8	18.2	18.5	18.7	19.0	19.3			−.04
					1	do	16.4	16.5	17.2	17.7	18.1	18.3	18.6	19.0	19.5	19.7	20.0			+.01
1311	9.7	19.7	69.3	Forged and annealed	1	do	16.0	16.0	16.7	17.3	17.7	18.0	18.4	18.7	19.1	19.5	20.0			
1312	10.4	20.7	67.5	do	1	do	15.9	16.0	16.6	17.1	17.5	17.8	18.3	18.6	18.9	19.4	19.9			+.01
1419	10.80	17.34	71.19	Quenched	1	do	16.4	16.7	17.1	17.6	17.9		18.4	18.8	19.0	19.2	19.5			+.02
1306	19.55	19.55	58.93	Cast	1	do		15.7	16.2	16.5	16.8	17.1	17.4	17.4				19.5	20.9	−.03
1306A				do	1	do	15.8	15.6	16.1	16.5	16.8	17.0	17.3	17.5				20.1	20.9	
					2	do		15.8	16.1	16.4	16.7	16.8	17.1	17.2	17.6	18.0	18.4			−.13
1303	19.80	7.76	69.30	do	1	do	17.4	17.5	18.2	18.6										+.00
					2	do				18.5	18.6	18.8	18.9	19.0				19.4	21.0	+.00
1310	20.2	7.9	69.6	Forged and annealed	3	do		17.7	17.9	18.2	18.4	18.5	18.9	18.8	19.0					−.09
					4	do	17.6	17.6	18.0	18.2	18.4		18.7	18.8	18.9	19.2	19.7			−.01
1295	27.78	18.50	50.30	Cast	1	do	18.5	18.4	18.4	18.6	18.8	18.9	19.1	19.2	19.4	19.9	20.6			+.03
					1	do	15.3	15.2	15.8	16.0	16.4	16.6	17.0					20.1	20.1	
					2	do			15.6		16.2	16.5	16.9	17.2	17.5	17.8	18.3			−.07
					3	do	15.0	14.8	15.3	15.8	16.0	16.3	16.7	16.9	17.3	17.6	18.1			+.01
																				+.00

1404	30.1	4.9	63.9	Hot-rolled	1	do	11.0	11.8	14.0	15.2	15.8	16.2	16.6	16.9	17.3	17.8	18.4			+.01
1304	36.0	16.4	47.4	Cast	1	do		13.8		15.2	15.7	16.1	16.4	16.7				19.8	20.8	−.04
					2	do		12.8	14.2	14.8	15.2	15.7	16.1	16.5	16.9	17.3				−.00
1291	40.3	21.1	34.6	do	1	do	14.1	14.0	14.7	15.1	15.5	15.8	16.2	16.5				19.0	19.9	−.06
					2	do		13.6	14.2	14.8	15.1	15.6	16.0	16.4	16.8					
1502	41.98	12.12	44.10	do	1	do	10.0	10.0	11.1	12.2	13.3	14.0	14.6					20.0	20.9	−.03
					2	do		8.7	9.1	10.8		13.0	13.7	14.4	14.9					
					3	do	8.8	8.7	9.2	10.7	11.9	12.8	13.6	14.2	14.7	15.3	15.9			−.01
1298	58.07	19.12	19.21	do	[1] 1	do	13.0	13.2	13.7	13.8	14.3	14.7	15.2	15.5				19.2	19.6	−.02
1305	61.00	15.70	20.26	do	1	do	12.2	12.3	12.7	13.3	13.7	14.1	14.5	14.7				17.8	19.1	−.04
					2	do				13.8			14.4		15.2					
1403	63.0	15.9	18.1	Hot-rolled	1	do	13.2	13.4	14.0	14.4	14.8	15.2	15.7	16.0	16.3	16.8	17.0			−.00
1301	65.22	16.23	15.33	Cast	1	do			13.3	13.5	13.9	14.3	14.7	15.0				18.2	19.1	
1313	70.1	16.3	6.6	do	1	do		13.6	13.8	14.0	14.3	14.6	15.0	15.2	15.3	15.6				[4] −.05

[1] Sample marked A represents duplicate of sample having same number.
[2] Coefficient of expansion is 10.0×10^{-6} between −50° and +20° C. and 11.0×10^{-6} between 20° and 250° C.
[3] Coefficient of expansion between 600° and 800° C. is 18.2×10^{-6}.
[4] Value obtained on duplicate sample heated from room temperature to 1,000° and cooled to room temperature.

Table 7 gives average coefficients of expansion of the 26 samples of nickel-chromium-iron alloys in this subsection. The table also indicates the phases (alpha and gamma) of the samples during the expansion tests.

An examination of Table 7 indicates that the coefficients of expansion of the nickel-chromium-iron alloys in the gamma phase are generally larger than the coefficients of the alloys in the alpha phase. The alloys in the gamma phase expand more than the same alloys in the alpha phase for the same temperature range. For the range from 20° to 400° C., the coefficient of expansion in the first heating (gamma phase) of the cast sample 1296 or 1296A is about 40 per cent larger than the coefficient in the second heating (alpha phase). The

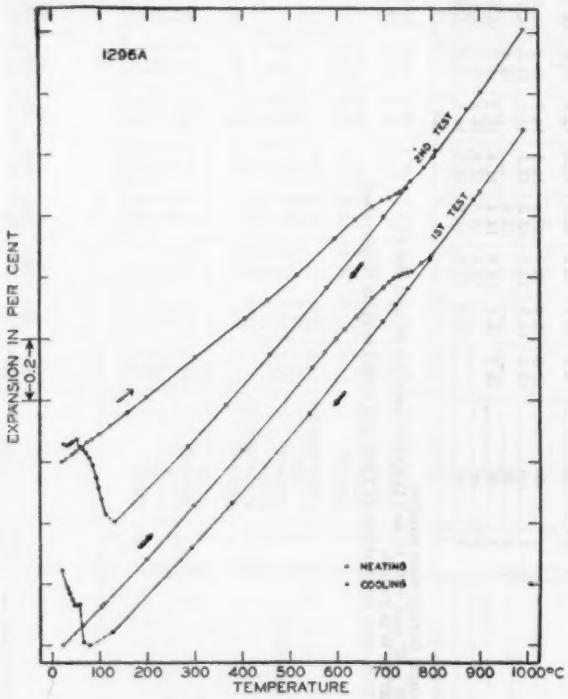

FIGURE 33.—*Linear thermal expansion of cast nickel-chromium-iron alloy (see fig. 34 for third test)*

Ni 8.41, Cr 21.66, Fe 64.63, C 1.15, Mn 1.16, Si 1.24, Al 1.57, Cu 0.10 per cent.

coefficients of expansion in the first heating (gamma phase) of the hot rolled sample 1411A are approximately 50 per cent larger than the coefficients in the second or third heating (alpha phase) to 500° C. These large differences in expansion were caused by phase changes.

In most cases the coefficients of expansion in the first heating of the cast nickel-chromium-iron alloys are larger than the corresponding coefficients obtained in the second or third heating.

A study of the average coefficients of expansion of the cast nickel-chromium-iron alloys for various temperature ranges indicates that the coefficients of expansion of the cast alloys containing less than 30 per cent nickel are larger than the coefficients of the cast alloys

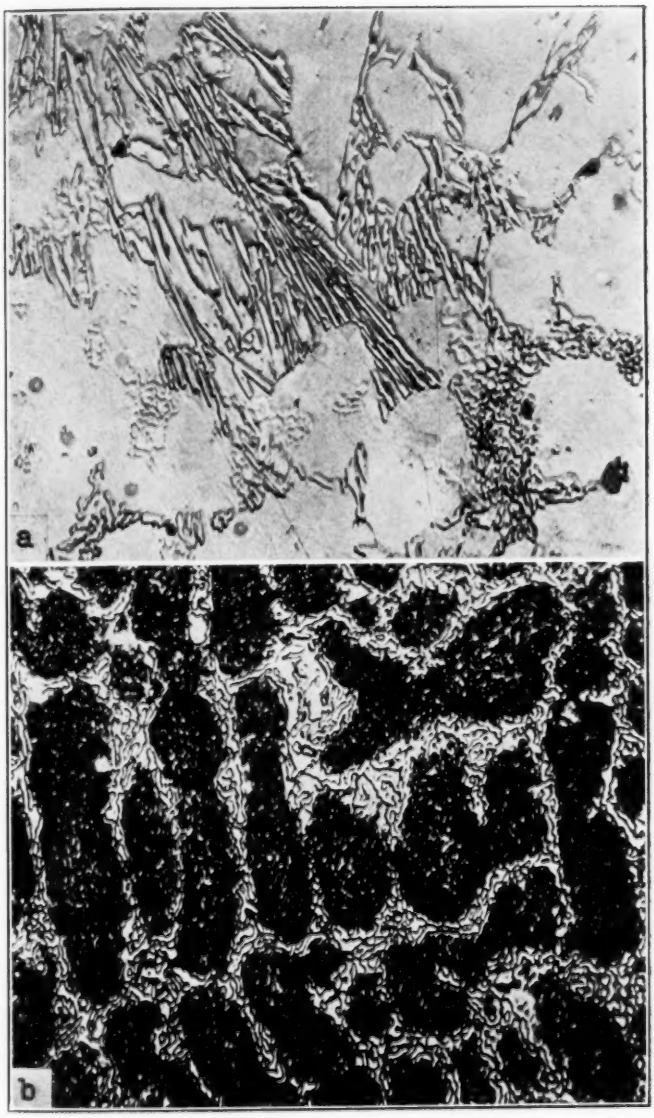

FIGURE 35.—*Microstructure of nickel-chromium-iron alloy (1296).* × *500*

Ni 8.41, Cr 21.66, Fe 64.63, C 1.15, Mn 1.16, Si 1.24, Al 1.57, Cu 0.10 per cent. *a*, As cast; *b*, after second expansion test.

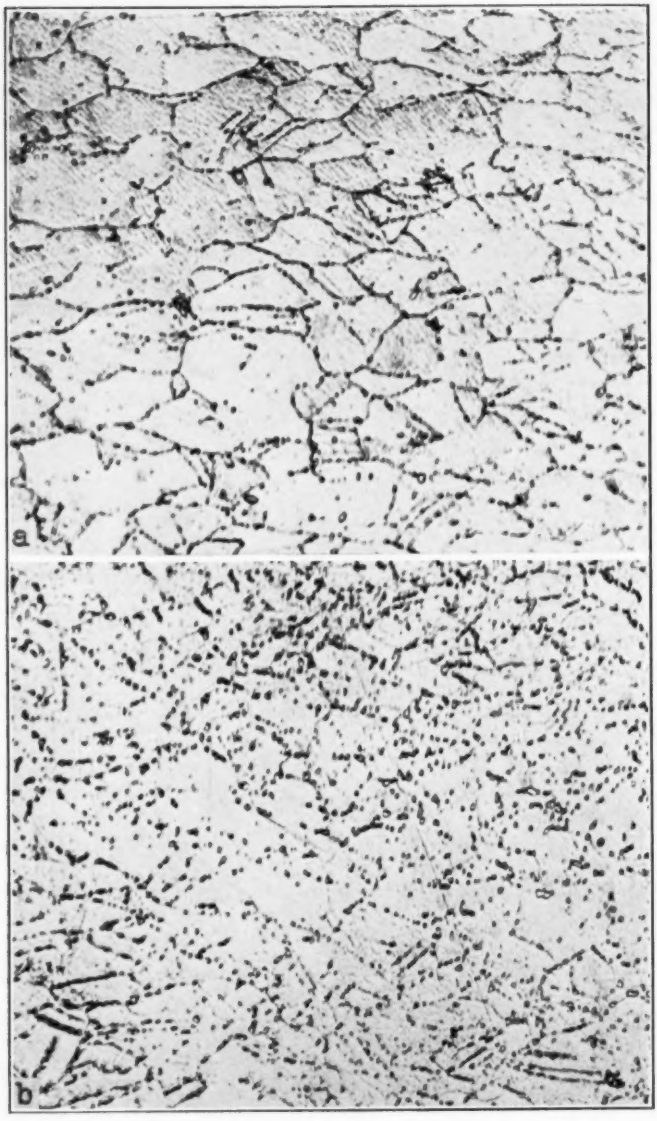

FIGURE 37.—*Microstructure of nickel-chromium-iron alloy (1297).* × *500*

Ni 7.80, Cr17.28, Fe 73.62, C 0.14, Mn 0.45, Si 0.28, Al 0.18, Cu 0.14 per cent. *a*, Hot-rolled and cooled in brine, annealed at 2,000° F. for one hour and air cooled; *b*, after expansion test.

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containing more than 30 per cent nickel. The coefficients of expansion of the former alloys decrease with increase in chromium content, but the coefficients of the latter increase with increase in chromium content.

A similar study of the average coefficients of expansion of the annealed nickel-chromium-iron alloys for various temperature ranges indicates that the coefficients of expansion of the annealed alloys containing from 0 to about 10 per cent nickel increase with increase in nickel content. The coefficients of expansion of the annealed alloys containing from about 10 to 30 per cent nickel decrease with

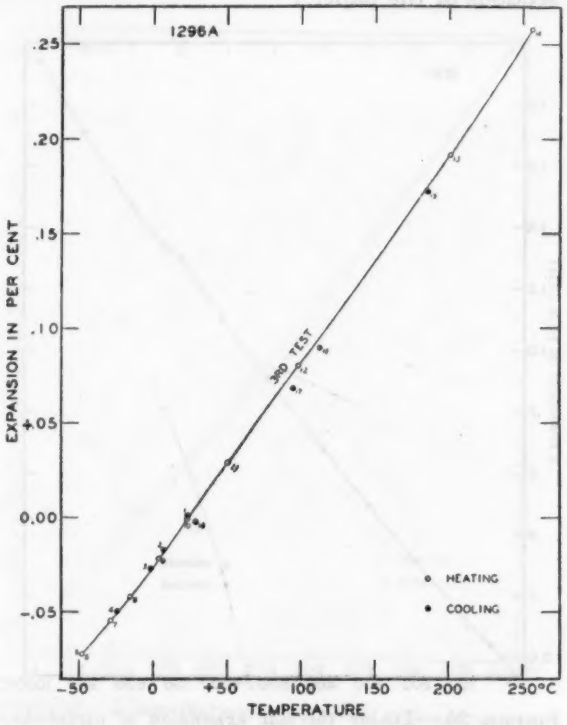

FIGURE 34.—*Linear thermal expansion of cast nickel-chromium-iron alloy at low temperatures (see fig. 33 for previous tests)*

Ni 8.41, Cr 21.66, Fe 64.63, C 1.15, Mn 1.16, Si 1.24, Al 1.57, Cu 0.10 per cent.

increase in chromium content, but the coefficients of the annealed alloys containing more than 30 per cent nickel increase with increase in chromium content.

The coefficients of expansion of the two quenched alloys in Table 7 are slightly larger than the annealed alloys which have the same approximate chemical composition.

V. CONCLUSIONS

The new data in this paper are useful in several ways: (*a*) It is possible to select heat-resisting alloys which have the same coefficients of expansion for a given temperature range as other materials;

for example, brass, copper, porcelain, steel, etc., when assembled in equipment or appliances where differences in expansion would be unfavorable. (*b*) It is possible to predict the coefficients of expansion of similar new alloys. (*c*) It is also possible to determine the heat treatment suitable for each type of alloy for a specific purpose as governed by the desired structure.

A comparison of the average coefficients of expansion found for the three groups of alloys (nickel-chromium, iron-chromium, and nickel-chromium-iron alloys) investigated is given in Table 8. (For values found for individual alloys reference should be made to the proper sections of the paper.)

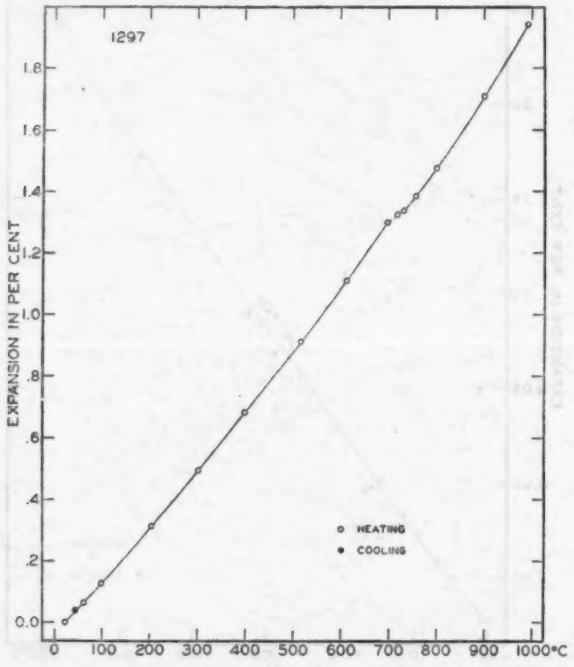

FIGURE 36.—*Linear thermal expansion of nickel-chromium-iron alloy*

Hot-rolled and cooled in brine; annealed at 2,000° F. for one hour and air cooled. Ni 7.80, Cr 17.28, Fe 73.62, C 0.14, Mn 0.45, Si 0.28, Al 0.18, Cu 0.14 per cent.

TABLE 8.—*Comparison of average coefficients of expansion of nickel-chromium, iron-chromium, and nickel-chromium-iron alloys*

Alloys	Chemical composition			Average coefficients of expansion per degree centigrade			
	Nickel	Chromium	Iron	20° to 60° C.	20° to 100° C.	20° to 200° C.	20° to 300° C.
	Per cent	*Per cent*	*Per cent*	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$
Nickel-chromium alloys	76.8–77.0	19.3–20.4	.....	13.1–13.8	13.0–13.6	13.3–14.0	13.3–14.3
Iron-chromium alloys	.....	17.0–24.6	74.0–81.7	9.7–10.5	10.0–10.6	10.3–10.8	10.6–11.1
Nickel-chromium-iron alloys	1.3–70.1	4.9–26.7	6.6–74.7	8.8–18.5	8.7–18.4	9.1–18.4	10.7–18.6

TABLE 8.—*Comparison of average coefficients of expansion of nickel-chromium, iron-chromium, and nickel-chromium-iron alloys*—Continued

Alloys	Average coefficients of expansion per degree centigrade—Continued						
	20° to 400° C.	20° to 500° C.	20° to 600° C.	20° to 700° C.	20° to 800° C.	20° to 900° C.	20° to 1,000° C.
	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$
Nickel-chromium alloys	13.9–14.5	14.7–15.1	15.3–15.7	15.8–16.2	16.2–16.7	16.7–17.2	17.2–17.8
Iron-chromium alloys	10.9–11.4	11.2–11.7	11.3–11.9	11.6–12.1	12.0–12.5	12.5–13.1	
Nickel-chromium-iron alloys	11.0–18.8	11.3–18.9	11.5–19.1	11.8–19.2	12.2–19.5	12.7–19.9	13.1–20.6

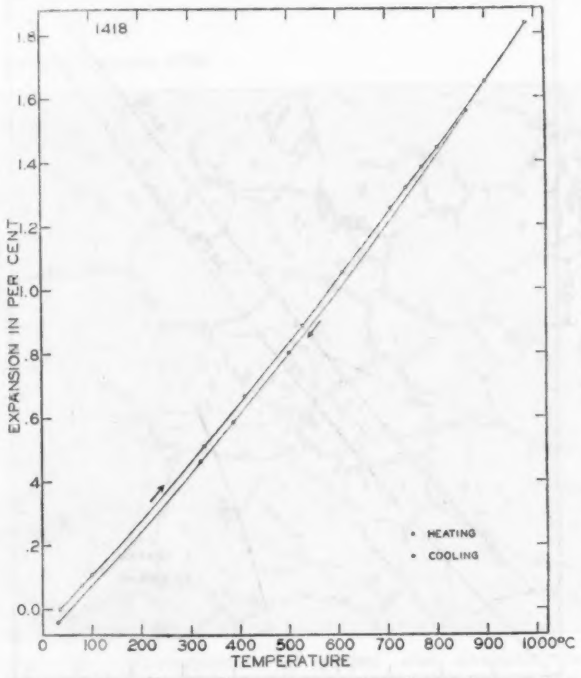

FIGURE 38.—*Linear thermal expansion of nickel-chromium-iron alloy*

Hot-rolled and annealed.
Ni 8.9, Cr 17.5, Fe 69.6, C 0.12, Mn 0.41, Si 0.37, P 0.017, S 0.016, Mo 3.08 per cent.

1. NICKEL-CHROMIUM ALLOYS

For a given temperature range, the coefficients of expansion of nickel-chromium alloys containing from 0 to about 20 per cent chromium are nearly the same.

2. IRON-CHROMIUM ALLOYS

Critical regions, due to transformations from alpha to gamma phase (austenite), were located. Transformations from alpha phase to austenite occur in carbon-free alloys containing from 0 to about 12 per cent chromium. In alloys containing about 0.05 per cent carbon, the austenite region extends from 0 to approximately 17 per cent chromium. With a carbon content of 0.74 per cent, a transformation

from alpha phase to austenite occurred in an alloy containing 24.6 per cent chromium. Carbon extends the austenite region into the richer chromium alloys.

The coefficients of expansion indicate a tendency to decrease slightly with increase in the chromium content of the iron-chromium alloys containing from 17.0 to 24.6 per cent chromium.

Figure 11 shows the effects of chromium content, carbon content, heat treatment, etc., on the coefficients of expansion of iron-chromium

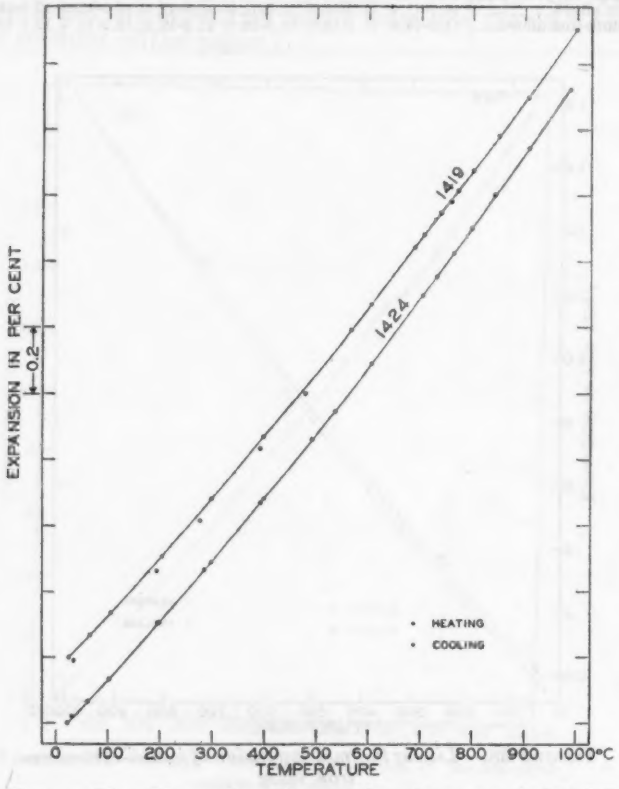

FIGURE 39.—*Linear thermal expansion of two quenched nickel-chromium-iron alloys*

1,424, Ni 9.6, Cr 17.7, Fe 72.0, C 0.06, Mn 0.36, Si 0.28, P 0.016, S 0.012 per cent.
1,419, Ni 10.80, Cr 17.34, Fe 71.19, C 0.06, Si 0.61 per cent.

alloys for various temperature ranges. The coefficients of expansion of annealed alloys (fig. 12) increase with temperature and generally decrease with increase in chromium content. For annealed alloys containing from about 12 to 25 per cent chromium, the changes in the coefficients of expansion are small.

3. NICKEL-CHROMIUM-IRON ALLOYS

The results on thermal expansion have been correlated with the structure of the alloys. Transformations from one phase to another caused significant changes in thermal expansion. The coefficients of expansion of the alloys in the gamma phase are generally larger than the coefficients of the alloys in the alpha phase.

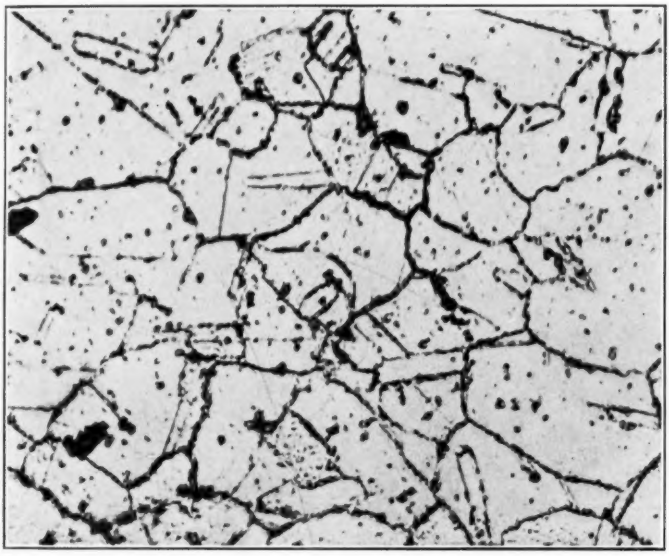

FIGURE 41.—*Microstructure of forged and annealed nickel-chromium-iron alloy after expansion test (1312).* × *500*

Ni 10.4, Cr 20.7, Fe 67.5, C 0.18, Mn 0.62, Si 0.56 per cent.

The first expansion curves of nearly all of the cast alloys indicate a retardation or decrease in expansion between 700° and 800° C., apparently due to precipitation of carbide. On repeated heating, these alloys do not show retardation or decrease in expansion, for the alloys appear to be stable after the precipitation of carbide in the first heating. In most cases, the coefficients of expansion in the first heating of the cast alloys are larger than the corresponding coefficients obtained in the second or third heating.

The coefficients of expansion of the cast nickel-chromium-iron alloys containing less than 30 per cent nickel are larger than the coefficients of the cast alloys containing more than 30 per cent nickel.

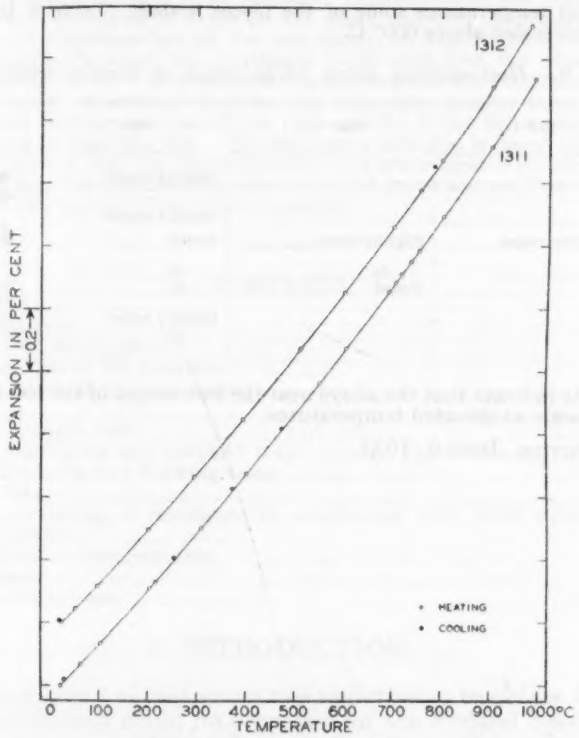

FIGURE 40.—*Linear thermal expansion of two forged and annealed nickel-chromium-iron alloys*

1,311, Ni 9.7, Cr 19.7, Fe 69.3, C 0.21, Mn 0.24, Si 0.89 per cent.
1,312, Ni 10.4, Cr 20.7, Fe 67.5, C 0.18, Mn 0.62, Si 0.56 per cent.

The coefficients of expansion of the former alloys decrease with increase in chromium content, but the coefficients of the latter increase with increase in chromium content.

The coefficients of expansion of the annealed nickel-chromium-iron alloys containing from 0 to about 10 per cent nickel increase with increase in nickel content. The coefficients of expansion of the annealed alloys containing from about 10 to 30 per cent nickel, decrease with increase in chromium content, but the coefficients of the annealed alloys containing more than 30 per cent nickel, increase with increase in chromium content.

VI. ACKNOWLEDGMENT

The author wishes to express appreciation to G. K. Burgess, H. W. Bearce, W. Souder, L. Jordan, and E. C. Groesbeck, of the National Bureau of Standards, for valuable suggestions, and to H. S. Krider, of the National Bureau of Standards, for assistance in the investigation.

NOTE.—Pieces cut from all of the samples in this investigation were heated in a furnace to 400° C., kept at this temperature for three hours, cooled slowly to room temperature and then the surface of each piece was examined. These pieces were successively heated to 500°, 600°, 700°, 800°, 900°, and 1,000° C., and the same procedure was carried out each time. No scale was observed on the surface of any of the pieces which had been heated to a temperature at or below 600° C. At higher temperatures some of the pieces scaled. Table 9 indicates the samples which scaled above 600° C.

TABLE 9.—*Heat-resisting alloys which scaled at elevated temperatures*

Sample	700° C.	800° C.	900° C.	1,000° C.
1297			Slightly scaled	Scaled.
1299				Slightly scaled.
1300 1300A			Slightly scaled	Do.
1303	Slightly scaled	Slightly scaled	Scaled	Badly scaled.
1310		do	do	Do.
1404		Scaled	do	Scaled.
1418				Slightly scaled.
1424			Slightly scaled	Scaled.
1427			do	Slightly scaled.

The results indicate that the alloys near the iron corner of the ternary diagram in Figure 1 scale at elevated temperatures.

WASHINGTON, June 9, 1931.

THE PHYSICAL PROPERTIES OF CAST STONE

By John Tucker, jr., G. W. Walker, and J. Arthur Swenson

ABSTRACT

The paper is a report of the results of tests made as a basis for the preparation of a Federal specification for cast stone. Samples representative of all the usual methods of fabrication, including a wide variety of aggregates, were studied. The compressive strengths varied from 1,550 to 21,720 lbs./in.^{2} and the 48 hours absorption varied from 2.0 to 13.1 per cent. The resistance of the material to freezing and thawing varied from complete destruction of the least resistant specimen in the twenty-fifth cycle to the most resistant specimen that first showed signs of disintegration at the one thousand four hundred and fiftieth cycle. Correlation between the resistance to freezing and the other physical properties was very poor. As a specification requirement the Schurecht ratio was the most valuable. Specimens that had an absorption greater than 6 per cent after five hours boiling were usually of poor quality if the Schurecht ratio was greater than 0.9 or less than 0.6. The Schurecht criterion is based upon a theoretical upper limit of 0.9, but the assignment of a lower limit is purely empirical. It is shown that the specification drawn for cast stone assures that any sample accepted will very probably be of good quality.

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I. INTRODUCTION

The present study of cast stone was undertaken to obtain data from which a specification could be prepared for the Federal Specifications Board. Moreover, published data on the physical properties of cast stone at the time the tests were begun were very meager, and the producers and users of this material had indicated that a knowledge of the properties would be of considerable interest to them.

The essential requirements for a cast stone are appearance, freedom from discoloration, and durability when exposed to weathering. Strength is relatively unimportant, and it may safely be assumed that if the material will resist disintegration by weathering action, it will be sufficiently strong for all other requirements. The appearance or texture is a matter of concern to the architect and may be covered by a statement to that purport in the specifications. The most serious discoloration is that due to efflorescence. This could be controlled far more effectively in cast stone, it is believed, by the prevention of

moisture penetration through the wall and the use of proper mortars than by an attempt to reduce the efflorescence by properties of the cast stone itself.

The weathering properties of a concrete may be, it is now currently believed, most accurately determined by freezing and thawing cycles repeated until disintegration occurs. Such tests, however, require a very long time for completion. It is desirable then to determine if a correlation exist between such resistance to disintegration and the results of tests that can readily be made within a short time in the laboratory, such as compressive strengths and absorptions. These physical properties were measured principally with the object of obtaining such a correlation.

The detailed data and description of test methods are being published in the 1932 Proceedings of the American Concrete Institute, volume 28.

II. SOURCE OF THE SAMPLES

A number of manufacturer's samples submitted to Federal departments were given to the bureau for tests, and in addition a number of manufacturers supplied samples upon request. Several samples were selected directly upon the building site by bureau representatives. The greater part of the samples was secured through the cooperation of C. G. Walker, secretary of the Cast Stone Institute.

III. DESCRIPTION OF THE SAMPLES

The samples tested included specimens made by the wet cast, dry tamped, puddled, and vibrated processes and of the faced and homogeneous types. The surface textures and colors of the samples varied over a wide range. Calcite, chiefly in the form of marble, was one of the most extensively used in a considerable variety of aggregates. Data were submitted by some of the manufacturers on the properties, material, method of casting, and curing conditions for a portion of the samples, but no direct data concerning the fabrication of the stone was obtained by the bureau.

IV. PREPARATION OF TEST SPECIMENS

One or more pieces slightly over 2 inches thick were cut from the samples. From these pieces six 2 by 2 inch cylinders were cored perpendicular to the face. The ends of three of the cylinders for the compression tests were ground until they were 2 ± 0.06 inches in height and finished to flat plane surfaces perpendicular to the axis. The three cores to be used in the freezing and thawing tests were so finished that no projections remained on any of the surfaces.

Three or more bars, approximately 1 by 1 by 8 inches in size, intended for the cross bending and the absorption tests, were cut from the samples and hand finished on the grinding lap.

Two-inch by two-inch prisms 4 inches long were also cut from a number of samples for modulus of elasticity determinations.

V. TESTS

1. STRENGTH TESTS

The samples were air-dry when received, but in cutting and grinding the test specimens to size they absorbed considerable water. A dry condition was selected as preferable to a saturated condition for test purposes because of cleanliness in handling specimens and the probable saving in time. The cylinders and bars for the strength tests were, therefore, dried for 72 hours at a temperature of 105° to 110° C. They were then immediately stored over calcium chloride in a desiccator at room temperature until tested.

Compressive tests were made on three 2-inch diameter cylinders cut from each sample. The 2 by 2 inch cylinder rather than a 2 by 4 inch cylinder was used because natural stone is usually tested in the form of 2-inch cylinders and because it was desired to include proportionately as much of the facing material as possible in the test specimen. The cylinders from faced cast stone were cut perpendicular to the face, and included all the facing and some of the backing. None of the specimens was capped nor was any material placed between the specimen and the upper or the lower bearing.

The cross bending specimens were tested by loading the midpoint of a 6-inch span, at the rate of 140 pounds per minute. The modulus of rupture was computed by the usual equation.

Three of the halves remaining after the modulus of rupture tests were cut to 2 inches in height within a tolerance of one-sixteenth inch, and the ends finished to flat surfaces perpendicular to the axis of the prism. These specimens were dried for 72 hours in an oven maintained between 105° and 110° C., then stored in the desiccator, and tested in compression with the axis of the prism perpendicular to the platen. The prisms were tested in addition to the cores, in order to determine the relative merits of the two forms of specimens for the purposes outlined in the introduction.

In addition, 2 by 2 inch prisms 4 inches long cut from a number of samples were used for the determination of the stress-strain relation. The strains were measured by two Tuckerman strain gages of 2-inch span mounted on opposite faces. The gages were attached to the prisms with elastic bands and rested on one-quarter by three-quarter inch rectangles of sheet aluminum fastened to the specimen with De Khotinsky cement.

2. ABSORPTION AND POROSITY TESTS

Three of the halves of the bars remaining after the cross-bending test were ground until they were approximately 3 inches long. These were dried at 105° to 110° C. until the loss in weight in 24 hours was not more than 0.1 per cent, then stored in the desiccator and the absorption determined after they had attained room temperature, by total immersion in distilled water maintained at room temperature. At the end of one-half hour, 2, 4, 6, 24, and 48 hours, the pieces were removed from the water, wiped with a damp towel, and weighed. The weight of water absorbed was assumed to be the difference between the wet weight and the dry weight.

After the 48-hour absorption period the specimens were kept in boiling water for five hours. Cold water was then run into the vessel

until room temperature was attained. The specimens were then wiped with a damp cloth and weighed. Afterwards they were weighed suspended in water. The total volume of water that had been absorbed when the specimens were boiled was taken as a rough measure of the total pore space, or porosity, and was computed by the equation:

$$P = 100\,\frac{W_b - W_d}{W_b - W_w}$$

where

P = apparent porosity, per cent.
W_b = weight of specimens after boiling.
W_d = weight of specimen when dry.
W_w = weight of saturated specimen suspended in water.

From most of the samples three more 1 by 1 by 3 inch prisms were cut for further absorption tests. These were dried in an electrically heated oven maintained at 65° C. through which a current of air, dried by passage through sulfuric acid, was passed. The drying was continued until the loss in weight during a 24-hour period was less than 0.1 per cent. The specimens were then immersed in water at 21° C., and the water boiled for five hours. Cool water was then injected into the boiler until room temperature was attained. The prisms were then removed one by one, the excess water wiped off with a damp towel, and the specimens immediately weighed. Following this, they were again placed in the 65° drying oven until the loss in weight was less than 0.1 per cent in 24 hours.

From each of 12 representative samples, three more 2 by 2 inch cores were cut. These specimens were placed in water at 21° C. for 24 hours and then placed in an electric-heated oven maintained at 35° C., through which a current of dry air passed. The drying was continued until the loss in weight of the specimens during a 24-hour period was less than 0.1 per cent. The specimens were then immersed in 300° F. oil (that used in railway signal lamps) maintained at 21° C. and the rate of absorption was obtained over a period of 48 hours. After this the specimens, while totally immersed in oil, were subjected to the reduced pressure of about 3 mm. of mercury absolute for five hours. The absorption was computed in terms of equivalent water absorption; that is, the weight of oil absorbed was divided by the specific gravity of the oil, thus giving the weight of water that would occupy the same space in the specimens that the absorbed oil occupied.

The use of these methods of drying at 35° or 65° in the process of determining the absorption was an effort to reduce or eliminate the loss of water of hydration of the cement that might occur through drying above the boiling point of water, to reduce or eliminate the consequent possible further hydration of the cement and also to reduce or eliminate the leaching out of some of the hydration products that might occur during the boiling in water. Any difference in the weight of water lost through drying at 35° or 65° C. and that lost through drying at 105° C. may be termed water of hydration.

3. FREEZING AND THAWING TESTS

The 2 by 2 inch cylindrical specimens prepared for the freezing and thawing tests were first immersed in water at approximately 20° C. for 48 hours. They were then started on cycles of alternate

freezing in an atmosphere maintained at −12° to −15° C. and thawing in a tank of water at room temperature. The specimens were invariably standing in one-fourth inch of water when placed in the freezing chamber so that the loss by evaporation from the surface of the specimen into the dry air of the chamber might be replaced by capillary rise from the water in the tray.

The specimens were examined at frequent intervals, particularly up to the first 100 cycles. Four states of disintegration were recorded:

First stage.—The number of the cycle at which the first sign of disintegration was noted.

Second stage.—The number of the cycle when the disintegration had progressed to the extent that an area equal to 1 cm^2 had spalled from the specimen.

Third stage.—The number of the cycle when the condition was such that the value of the stone for facing would be utterly destroyed.

Fourth stage.—The number of the cycle when at least one-third of the specimen was destroyed, or when the strength had been so reduced that complete disintegration would have occurred within a few more cycles.

Some specimens (which had previously not shown any signs of disintegration) developed such severe failure during a single cycle as to warrant them being classed in the second or third stages. In such cases the arrival of the first and second (or third) stages is represented by the same number of cycles.

The measurement of the disintegration by such a method is governed solely by the judgment of the observer, and is open to the objection that two observers might disagree as to the exact number of cycles at which any one specimen should be advanced from one stage to the next. Another method of measuring the disintegration would be to weigh the specimens and advance them from stage to stage according to loss in weight. This latter method, however, has the very serious disadvantage of giving no weight to the appearance of the stone nor the kind of disintegration. For example, a surface layer of one-eighth inch in thickness might come from off a sample of cast stone, leaving the fresh surface practically as satisfactory in appearance as the original surface, whereas the surface of another stone might pit and present a very poor appearance with the loss of much less material. As another illustration, one sample cracked into two pieces. By the weight criterion this would have been a large loss, yet in a building, if the crack occurred in a direction almost perpendicular to the face, the appearance and utility of the piece would not be appreciably affected.

The number of cycles at which the first signs of disintegration occurred were capable of closer measurement and, therefore, were more accurately determined than for the succeeding stages. Since these first signs of disintegration were most accurately determined it may appear wasteful of time and energy to have continued the tests beyond this point. The amount of disintegration that was first observed, however, was usually so small that the value of the stone was practically unchanged. It was therefore necessary to continue the tests until appreciable disintegration occurred, in order to obtain data that would be of value in showing the relative resistance of the various samples up to the point where the value of the

material as facing for building had been largely destroyed by the freezing and thawing tests. An arbitrary combination of the number of cycles for each of the four stages was used as a means of comparing the resistance of the samples to disintegration. For convenience this is called the mean resistance, and is computed as follows:

$$\text{Mean resistance} = A + 0.95\ (B - A) + 0.50\ (C - B)$$

Where

A is the number of cycles when the first stage is reached.
B is the number of cycles when the second stage is reached.
C is the number of cycles when the third stage is reached.

VI. TEST DATA

Since not more than three tests were made for the determination of each property, reliable information could not be gained as to the relative accuracy with which test results could be repeated for the different samples. However, an estimated modulus of precision for each type of test determination has been given in Table 1.

To show the distribution of the values of the more important test measurements the histograms of Figures 1 to 4 have been prepared. The averages of the tests of all specimens from each sample, and not the individual test results, were used in preparing these figures.

TABLE 1.—*Precision measures*

	Compressive strength		Modulus of rupture	Water absorption (in per cent of dry weight)			Schurecht ratio
	2 by 2 inch cylinders	1 by 1 by 2 inch prisms		48 hours at room temperature	48 hours plus 5 hours boiling	5 hours boiling after 65° C. drying	
	Lbs./in.²	*Lbs./in.²*	*Lbs./in.²*				
Minimum	1,550	1,300	220	2.0	2.5	3.0	0.39
Maximum	21,720	15,780	1,640	13.1	18.2	17.2	1.00
Standard deviation [1] (σ)							.08
Coefficient of variation [2] (Cv) per cent	10	23	21	10	7	8	

	Porosity	Apparent specific gravity	300° oil absorption (in per cent of dry weight)			Resistance to disintegration	
			½ hour	48 hours	48 hours plus 5 hours vacuum	Final stage	Mean resistance
	Per cent					*Cycles*	*Cycles*
Minimum	6.7	1.80	0.4	1.6	2.4	25	25
Maximum	32.7	2.66	8.4	9.2	13.4	[1] (1,730)	[1] (1,345)
Coefficient of variation [2] (Cv) per cent	6	2	16	12	10	30	29

[1] At the number of cycles indicated the samples had not reached the final stage. That with 1,545 cycles had not reached the second stage.

[2] Whichever constant shows least variation through the range from low to high, has been given. The parameters are for individual specimens; for porosity they have been computed from the precision of the measurements from which the porosity was computed.

The prism strengths varied from 1,300 to 15,780 lbs./in.^{2} The higher values are considerably more than the strengths ordinarily obtained in concrete, strengths of the latter greater than 6,000 lbs./in.^{2} being rare. Concrete specimens, however, are ordinarily tested in a moist condition, whereas the strength tests in the present case were made upon well-dried specimens. The samples with strengths above 12,000 lbs./in.^{2} according to the manufacturer, were molded by the vibration process and were then steam cured. The strength of one sample, 15,780 lbs./in.^{2} is extremely high for concrete of as lean a mix as the appearance of the sample would indicate. The cylinder strengths, as was to be expected from the difference in ratio of height

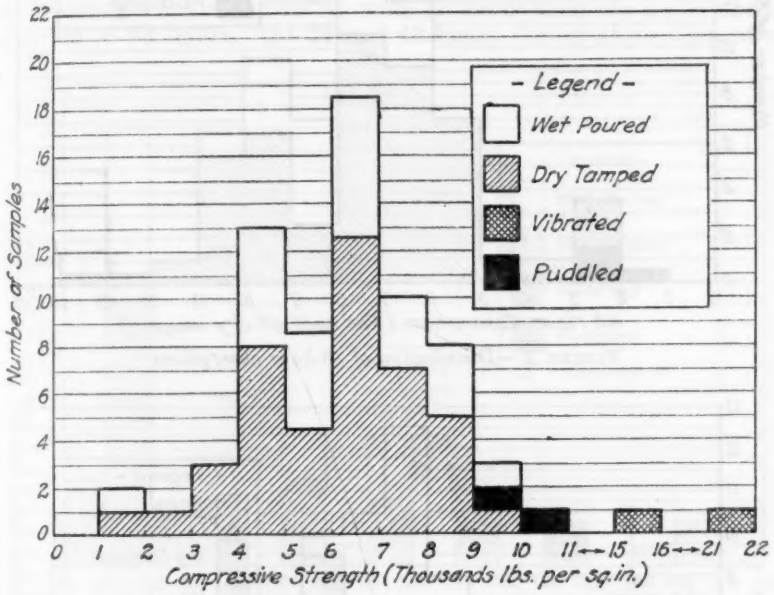

FIGURE 1.—*Distribution of compressive strength of 2 by 2 inch cylinders*

to area of cross section, were greater than the prism strengths. They varied from 1,550 to 21,720 lbs./in.^{2}, the distribution of the strengths being given in the histogram of Figure 1.

The modulus of ruptures varied from 220 to 1,640 lbs./in.^{2}, which is not as great a proportional range of variation as for the compression test results. This is to be expected from the results of flexural tests that have been made on concrete beams.

It is to be noted that the samples of concrete with the two highest compressive strengths were, respectively, fifth and thirteenth in order of modulus of rupture strength. This difference in order is probably due to the vibration method of fabrication of these specimens which causes "close packing" of the aggregate, markedly increasing the compressive strength but not increasing the cross bending strength by nearly so large a percentage. The distribution of the prism and cylinder compressive strengths (see fig. 1) and the cross bending strengths of the dry tamped specimens is very nearly the same as that of the wet poured specimens.

The absorptions following drying at 105° to 110° C. exhibit the same wide variation as the strengths. The 2.0 per cent water absorp-

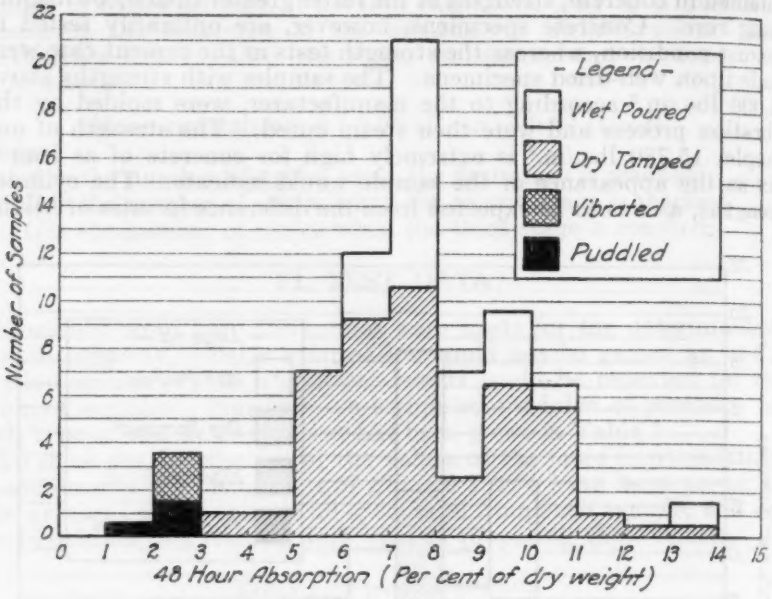

FIGURE 2.—*Distribution of 48-hour absorptions*

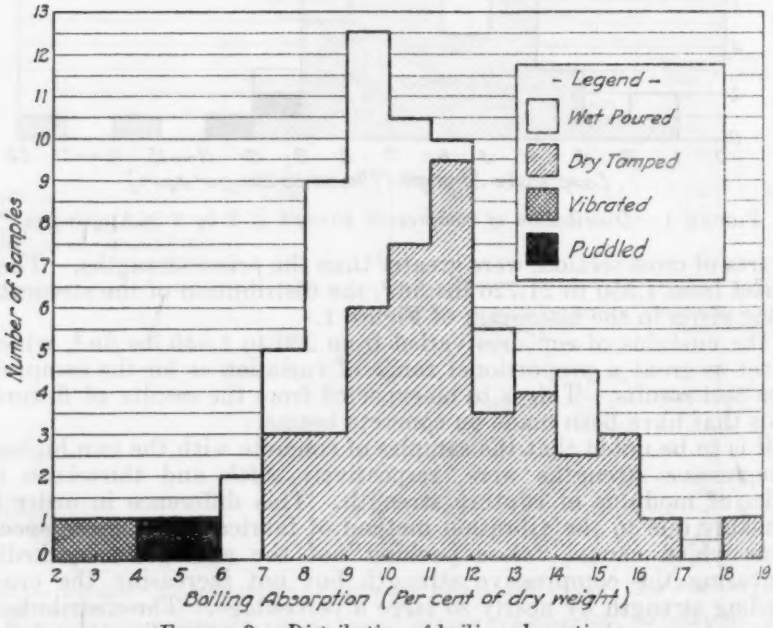

FIGURE 3.—*Distribution of boiling absorptions*

tion of specimen BG at 48 hours and the 2.5 per cent absorption of specimen BY after 48 hours in cold water and 5 hours in boiling

water are unusually low values for concrete made with ordinary aggregate. The cold-water absorptions of the tamped specimens is in general lower than the absorption of the poured specimens. (See fig. 2.) In the boiling absorption, however, the tamped specimens average higher than the poured, thus reversing the order. (See fig. 3.) The strengths and absorptions are roughly related to each other, for, in general, the higher the strength the lower is the absorption.

Only 45 samples were dried at 65° C. and boiled for five hours. Absorption values ranging from 3.0 to 17.2 per cent were obtained, and in every case the absorption was less than that obtained by drying at 105° to 110° C. followed by 48-hour water immersion and subsequent 5-hour boiling. The equivalent water absorptions in 300° oil following a drying at 35° C. were all lower than the water absorptions up to six hours. At 24 and 48 hours the oil absorption of one

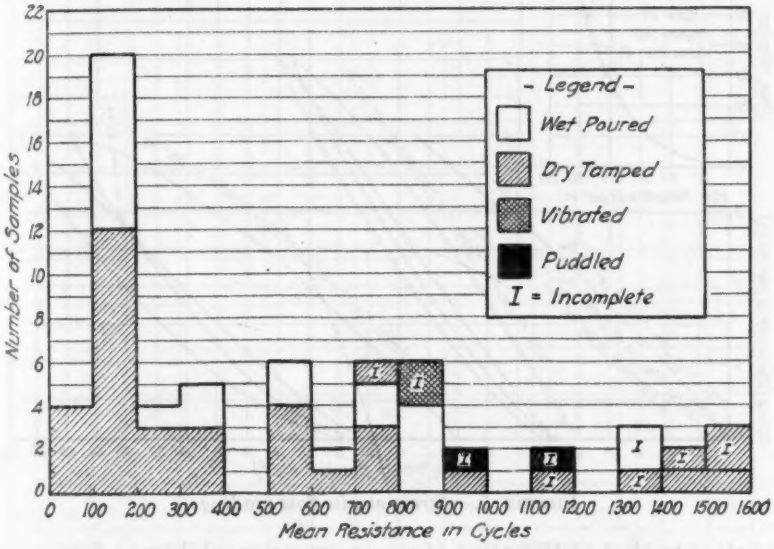
Number of Samples
Mean Resistance in Cycles
- Legend -
Wet Poured
Dry Tamped
Vibrated
Puddled
I = Incomplete
0 2 4 6 8 10 12 14 16 18 20 22
0 100 200 300 400 500 600 700 800 900 1000 1100 1200 1300 1400 1500 1600

FIGURE 4.—*Distribution of resistance to freezing and thawing*

specimen (BF) was more than the water absorption at similar intervals, although the boiling absorption was greater than the oil absorption under vacuum. These special tests indicate that the absorption values include factors other than simple filling of the voids with water, since part of the water lost and regained is probably water of hydration. Furthermore, the values were in no better accord with the resistance to freezing and thawing than those obtained by the more commonly used methods.

The range in resistance to freezing and thawing is proportionately larger and even more remarkable than the range in the strengths and the absorptions. (See fig. 4.) Sample BM showed the least resistance, the first sign of disintegration being noted at the twenty-second cycle and complete disintegration occurring at the twenty-fifth cycle. This sample had the lowest compressive and cross bending strengths and the highest absorption up to 48 hours, and would, a priori, be expected to have a low resistance. Sample E was the

most resistant, showing the first signs of disintegration at the one thousand four hundred and fiftieth cycle, but did not have outstanding physical characteristics that would indicate such a high resistance. It is to be noted that the wet-poured and dry-tamped specimens are equally distributed in their resistance to disintegration, and that the specimens made by puddling and by the vibration method are above the average resistance.

The properties of the two puddled concrete specimens, particularly the high strengths and the low absorptions, would indicate that they were made from a rich mix (as verified by the maker's statement of the proportions) with a moderate water content, and of a plastic consistency, very different from the consistencies used in the dry-tamp and wet-pour processes. It is probable that the consistency

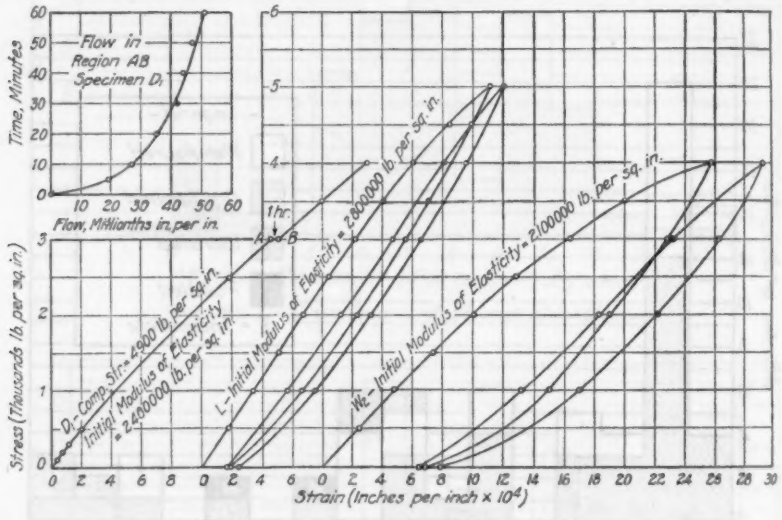
Time, Minutes
Flow in Region AB Specimen D1
Flow, Millionths in. per in.
Stress (Thousands lb. per sq. in.)
Strain (Inches per inch x 10⁴)
1 hr.
A
B
D1 - Comp. Str. = 4900 lb. per sq. in. Initial Modulus of Elasticity = 2,600000 lb. per sq. in.
L - Initial Modulus of Elasticity = 2,800000 lb. per sq. in.
W2 - Initial Modulus of Elasticity = 2,100000 lb. per sq. in.

FIGURE 5.—*Stress-strain-flow readings*

was close to that at the point of minimum permeability as determined by Glanville.[1]

It was observed that none of the specimens used in the absorption or freezing and thawing tests showed any signs of staining or efflorescence.

Stress-strain measurements were made on 15 oven dried 2 by 2 inch prisms 4 inches high cut from 11 of the samples. Some of these results are shown in Figure 5. The strain measurements were made with a Tuckermann gage on a 2-inch length and were carried close to the compressive strength of the material. The initial modulus of elasticity values ranged from 1.3 to 3.2 million pounds per square inch, values that are not divergent from those ordinarily to be expected from concrete.

Repeated loadings were made on most of the specimens, and on specimen D_1 time flow measurements were made for one hour. The load on this specimen was maintained at 3,000 lbs./in.^{2} or 61 per cent of the 4,900 lbs./in.^{2} ultimate strength of the specimen. In an hour

[1] Glanville, W. H., Building Research Technical Paper No. 3 of the Department of Scientific and Industrial Research, Great Britain.

the measured flow was 0.00005 in./in. The repeated loading curves showed the usual hysteresis loops.

Although the strain readings that were made are of no direct importance in indicating the quality of the material to withstand weathering, they are of sufficient interest in themselves to warrant presentation here. The measurements are also interesting in showing the delicacy of the Tuckermann gage. To obtain the full advantage of the precision of this gage the readings should be made in a constant temperature room.

VII. THE CORRELATION OF RESISTANCE TO WEATHERING WITH OTHER PHYSICAL PROPERTIES

The important physical property of cast stone is its resistance to destruction by weathering. The other physical properties are of

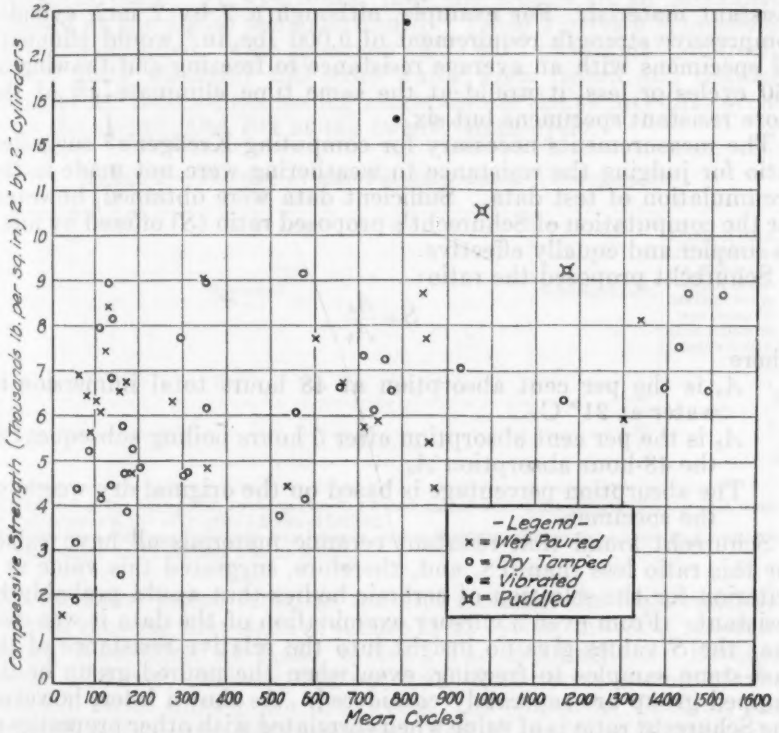
Compressive Strength (Thousands lb. per sq. in.) 2" by 2" Cylinders
Mean Cycles
0 100 200 300 400 500 600 700 800 900 1000 1100 1200 1300 1400 1500 1600
0 1 2 3 4 5 6 7 8 9 10 11 15 16 21 22
-Legend-
× = Wet Poured
○ = Dry Tamped
● = Vibrated
⌘ = Puddled

FIGURE 6.—*Compressive strength compared to mean resistance to freezing*

minor importance except for the possibility of their use in indicating this resistance. The effects of the freezing and thawing tests should not, a priori, be expected to be identical with the effects of outdoor exposure causing the disintegration that is known as weathering. Materials placed out of doors are subjected to natural weathering processes other than the freezing and thawings of entrained water. Alternate soaking and drying probably also produces disintegration. Large and fairly rapid changes in temperature, such as occur between days of strong sunshine and cool nights, are ascribed by geologists as

the cause of the exfoliation of granite boulders. Crystallization of salts in the pores of materials may be an additional cause of disintegration. However, in lieu of any more satisfactory test and because actual weathering tests would require a minimum of several decades for the accumulation of satisfactory data, the freezing and thawing tests were accepted as a standard in the present analysis.

The half-hour and the 48-hour absorptions as well as the porosities show practically no correlation with resistance to destruction. The boiling absorption, that is, the absorption after 48 hours followed by 5 hours boiling, shows a slight trend of increasing resistance with decrease in absorption. There is a slightly better correlation between cylinder strength and resistance as shown in Figure 6; the correlation between prism strength and resistance is not superior to that shown in Figure 6. However, the correlation of any of the strengths, or of the boiling absorption, with the resistance to freezing is so low that these criteria are of no direct practical value for the selection of a resistant material. For example, although a 2 by 2 inch cylinder compressive strength requirement of 9,000 lbs./in.^{2} would eliminate all specimens with an average resistance to freezing and thawing of 150 cycles or less, it would at the same time eliminate all of the more resistant specimens but six.

The measurements necessary for computing Kreüger's [2] suggested ratio for judging the resistance to weathering were not made in the accumulation of test data. Sufficient data were obtained, however, for the computation of Schurecht's proposed ratio (S) offered by him [3] as simpler and equally effective.

Schurecht proposed the ratio:

$$S=\frac{A_c}{A_b}$$

where

A_c is the per cent absorption at 48 hours total immersion in water at 21° C.

A_b is the per cent absorption after 5 hours boiling subsequent to the 48-hour absorption A_c.

The absorption percentage is based on the original dry weight of the specimen.

Schurecht found that resistant ceramic materials all have values for this ratio less than 0.8, and, therefore, suggested this value as a criterion for the selection of ceramic bodies that would probably be resistant. From even a cursory examination of the data it was seen that the S values give no insight into the relative resistance of the cast-stone samples to freezing, even when the poured group or the tamped group are seperately considered. As shown later, however, the Schurecht ratio is of value when correlated with other properties of the cast stone.

All but four of the poured specimens have Schurecht ratios above 0.75, and all but four of the tamped specimens had values below 0.8. More than half of the wet poured specimens have values for S that would indicate poor resistance while only three of the dry-tamped specimens have values of S which indicate inferior quality. Nevertheless, as may be seen from Figure 4, the poured and tamped speci-

[2] H. Kreüger, Trans. of the Royal Swedish Inst. for Scientific and Industrial Research, Stockholm, No. 24; 1923.

[3] L. A. Palmer and J. V. Hall, Proc., A. S. T. M., vol. 30, Pt. II; 1930.

mens were of approximately equal average resistance to freezing and thawing cycles.

The reader is referred to a paper entitled "The Selection of Durable Aggregate for Concrete," [4] for comments on Kreüger's and Schurecht's criteria as applied to stone and to slag of a size suitable for use as large aggregate in concrete. In that paper it was shown that these criteria are of no value in indicating the resistance of an aggregate to freezing and thawing tests. The porosity of the aggregates was, however, much lower than that of the greater part of the cast-stone specimens included in the present tests.

Portions of the 1 by 1 inch prisms of five samples were ground down until each weighed approximately 150 g. They were dried at 105° to 110° C. to constant weight and the 48-hour 21° C. water absorption determined. The specimens were then subjected to freezing and thawing cycles. Weighings of the specimens were made up to the thirty-fifth cycle. It was found that the weight of all specimens increased as the cycles were continued. Table 2 gives a synopsis of the results obtained. One specimen (AU) with an original Schurecht ratio of unity absorbed still more water when frozen and thawed. Specimen AC reached the boiling absorption at the twenty-first cycle, BF at the eighth, and BG at the twenty-sixth cycle.

TABLE 2.—*Increase in absorbed water due to freezing cycles*

Specimen	Schurecht ratio	Cycle of freezingand thawing at which the weight of absorbed water was equal to that following 5 hours boiling
AC	0.53	21
AF	.57	(1)
AU	1.00	[2] 0
BF	.48	8
BG	.49	26

[1] At the end of the thirty-fifth cycle specimen AF had gained 0.84 of the weight of water that would have been present in the voids after 5 hours of boiling.

[2] This specimen continued to absorb water slowly, and at the thirty-fifth cycle had absorbed 7 per cent more water than it contained after 5 hours boiling.

No specimen tested failed in the first freezing, the least resistant specimen showing first signs of failure in 22 cycles, the most resistant showing first signs at 1,450 cycles. The Schurecht or Kreüger criteria, however, indicate the potential destructive action of the entrained water during the first cycle. As shown in Table 2, the entrained water constantly increases, and if the S or K ratios be applied, they must be determined for each increasing cycle. The problem is further complicated in that the relative amounts of the entrained water that is mechanically held and that is chemically combined is unknown.

Since the resistance to disintegration by freezing and thawing has been shown to be practically independent of the absorption and therefore the porosity, we may conclude that the destruction is probably not solely due to the internal pressure of the contained ice. It should

[4] Rock Products; Aug. 1, 1931.

be noted carefully, however, that the stresses caused in the material by the pressure of the ice, will possibly depend on the pore shape as well as the relative pore space. It may well be that Kreüger's ratio or some other absorption measurement may give an empirical indication of this shape and so prove of value in indicating the resistance to freezing and thawing tests.

The simpler physical tests having failed to give a definite indication of the resistance to destruction by freezing, the cast-stone samples were carefully examined for structure and for mineral composition of the aggregates. The type of aggregate or the combination of aggregates present in the test specimens apparently has no important influence on the resistance. For example, samples A, C, D, and E had very similar values for compressive strength, absorption and Schurecht's ratio, and all but one had practically the same modulus of rupture. However, samples D and E were highly resistant, while A and C showed very low resistance. Sample E was fabricated by the dry-tamp process; the others were wet-poured. Samples C and E, one poor, the other very good, had only one material, calcite, as aggregate. Samples A and D had calcite and slag as aggregate, yet in resistance to freezing and thawing one was poor, the other very good. The whole list of samples may be examined and it will be found, as with these four samples, that the materials made with any particular type of aggregate show no definite superiority in relation to the other samples.

The spalling of small particles from the surface was usually the first sign of the effects of the freezing and thawing cycles. This could have been due to the internal pressure of newly formed ice or, more probably, to the differential expansion due to temperature differences or to both effects. The main disintegration, however, which bore no relation to the initial spalling, consisted in a separation of the aggregate from the cement and fine aggregate mortar. Initial signs of the ultimate failure usually consisted in the appearance of raised "map" lines around the portions of aggregate exposed on the surface. The concrete was found to have separated along this line, and as the freezing cycles progressed, it would rise higher along one side of the line of separation than the other until eventually a portion on the higher side would separate completely from the remainder. Examination of such a piece and the surfaces of separation indicated that the separation was accompanied by a destruction of the bond of the mortar to the aggregates.

VIII. SPECIFICATION REQUIREMENTS

The time required to determine weathering resistance by repeated freezing and thawing is so great that it is not practicable to use this test as a specification requirement. Simpler physical tests which can be made within a week must be used. Unfortunately such tests show individually a low correlation with the results of the cyclic freezing and thawing tests. Consequently, the specification must be based upon several requirements, which together will exclude a large proportion, if not all, of the materials having a low weathering resistance.

It may happen that some samples which have shown satisfactory weathering qualities (as determined by the freezing and thawing test) may also be excluded. This is unfortunate, but the exclusion of poor material is the fundamental objective of the specification.

The requirement of a minimum compressive strength of 5,000 lbs./in.^{2}, of a maximum 48-hour absorption of 8 per cent, and of a maximum boiling absorption (48 hours soaking at room temperature followed by five hours boiling) of 11 per cent eliminated a large number of the specimens with poor weathering qualities.

While seeking an additional criterion of rejection, it was noted that a large portion of the poor samples that had not been rejected had Schurecht ratios below 0.6 or above 0.9. It was also noted that most of the good samples in this category had low absorptions. The requirements of a Schurecht ratio of not less than 0.6 nor more than 0.9 was, therefore, added with the condition that it be applied only to those specimens whose boiling absorption was more than 6 per cent. The use of a lower limit for the Schurecht ratio has no theoretical foundation, but the results of these and other tests have shown that neither does an upper limit apply theoretically. Both were used solely because they were the only criteria found for separating a number of the specimens of good quality from those of poor quality that could be differentiated by no other means.

The specification as written eliminated all specimens (12) showing a weathering resistance of less than 113 mean weathering cycles, and all but two of the specimens (28) showing a weathering resistance less than 280 cycles. On the other hand, 21 specimens with a resistance of 300 cycles or over were excluded. Of the 68 specimens upon which all specification tests were made 19 met the requirements of the specification and 49 were rejected.

IX. SUMMARY

1. The compressive strength of the 2 by 2 inch cylinders varied from 1,550 to 21,720 lbs./in.^{2}; the compressive strengths of 1 by 1 by 2 inch prisms varied from 1,300 to 15,780 lbs./in.^{2}

2. The modulus of rupture determined on 1 by 1 by 8 inch bars on a 6-inch span varied from 220 to 1,640 lbs./in.^{2}

3. The 48-hour absorption in water at room temperature varied from 2.0 to 13.1 per cent of the dry weight, and after then boiling the specimens for five hours the absorptions ranged from 2.5 to 18.2 per cent.

4. There was no marked difference in the distribution of the strengths, the 21° C. absorptions, or the resistance to destruction by freezing and thawing between the specimens made by the wet-cast and those made by the dry-tamped process. The boiling absorption of the dry-tamped specimens averaged higher than those of the wet-cast specimens.

5. The two samples made by the vibration process were very high in compressive strength and above the average in cross-bending strength. The absorptions were much below the average, the resistances to freezing and thawing above the average.

6. The two samples made by puddling possessed the highest cross-bending strengths and, other than the vibrated specimens, had the highest compressive strengths. Like the vibrated specimens, the absorptions were very low, and the resistance to freezing and thawing above the average.

7. The Schurecht ratios of the dry tamped specimens were almost all lower than those of the poured specimens. The Schurecht ratio

in itself gave no indication of the quality of the materials for resistance to disintegration, but the far greater portion of these specimens with an absorption due to five hours boiling of more than 6 per cent and with a Schurecht ratio higher than 0.9 or lower than 0.6, were of poor resistance.

8. Repeated freezing and thawing in which the specimen is constantly in contact with water results in the absorption of more and more water. The specimens within a short time, therefore, are all thoroughly saturated with water and the internal stresses produced by the cycles from this point of saturation onward must be independent of the initial Schurecht or Kreüger ratio.

9. There is not sufficient correlation of the resistance to freezing and thawing of the specimens with their strength and porosity to indicate that failure is due in any large measure to destruction by internal ice pressure.

X. ACKNOWLEDGMENT

The authors desire to express their appreciation of the assistance of Ward Pigman for identification of the mineral composition of the aggregates and other assistance in the preparation of the paper.

WASHINGTON, April 15, 1931.

INVESTIGATIONS OF KENNELLY-HEAVISIDE LAYER HEIGHTS FOR FREQUENCIES BETWEEN 1,600 AND 8,650 KILOCYCLES PER SECOND[1]

By T. R. Gilliland, G. W. Kenrick, and K. A. Norton

ABSTRACT

The results of observations of the height of the Kennelly-Heaviside layer carried out near Washington, D. C., during 1930 are presented. Evidence for the existence of two layers (corresponding closely in virtual height to the E and F regions discussed by Professor Appleton) is found during daylight on frequencies between three and five megacycles. The modification in the virtual height of the higher F layer produced by the existence of a low E layer is investigated theoretically, and the possibility of large changes in virtual height near the highest frequency returned by the E layer is pointed out. A number of oscillograms showing the characteristic types of records observed during the tests are presented together with a graph of average heights from January to October, 1930.

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I. INTRODUCTION

It is the purpose of this paper to describe tests conducted by the National Bureau of Standards for the study of the Kennelly-Heaviside layer subsequent to those recently reported.[2] The method employed in these tests is the group retardation or pulse method described by Breit and Tuve.[3] In this method pulses of about 5×10^{-4} second duration are transmitted with a group frequency of about 30 pulses per second. The signals received at a distant point are recorded by means of an oscillograph.

Fig. 1 (*a*) shows the rectified form of the pulse as received in the absence of sky waves. Received patterns showing more than one peak for a single transmitted pulse are attributed to waves arriving over more than one path; that is, a ground wave and single or multiple reflections from one or more ionized strata or layers. Patterns indicating reflections are shown in Figure 1 (*b*).

The pulse method has been extensively employed in America in Kennelly-Heaviside layer studies. In England, phase interference

[1] Presented at annual meeting of American Section, International Scientific Radio Union, May 1, 1931.
[2] T. R. Gilliland, Kennelly-Heaviside Layer Height Observations for 4,045 kc. and 8,650 kc., B. S. Jour. Research, vol. 5, RP246, p. 1057; 1930, and Proc. I. R. E., vol. 19, p. 114; 1931. P. A. DeMars, T. R. Gilliland, G. W. Kenrick, Kennelly-Heaviside Layer Studies, Proc. I. R. E., vol. 19, pp. 106–113; January, 1931.
[3] G. Breit and M. A. Tuve, A Test of the Existence of a conducting Layer, Phys. Rev., vol. 21, p. 554; 1926; and Proc. I. R. E., vol. 17, p. 1513; 1929.

methods have been used by Prof. E. V. Appleton and coworkers.[4] It is of interest to note the good accord of the results obtained by the methods outlined here with those of Professor Appleton.

Both methods have peculiar advantages, and, as has been emphasized, depend upon somewhat different analytical relations for their interpretation. It has been shown, however, that the results obtained by both methods should be in accord.[5] A brief review and comparison of the methods follows; the reader is referred to the references noted for a more extended discussion.

Briefly, Appleton's method utilizes the phase reinforcements and cancellations produced by slight changes in emitted frequency due to the presence of multiple transmission paths having different phase retardations (that is, due to sky waves). The group retardation observations, on the other hand, measure the time retardation between the pulses arriving over different paths. The Appleton method employs balanced open antenna and loop antenna systems which permit measurements of polarizations and other phenomena not directly disclosed by group retardation studies when a nondirectional antenna is employed. However, directional antennæ may be used to advantage to obtain additional information when pulse methods are employed. An interesting preliminary application of pulse methods to a study of phase relations has been described.[6] During the observations described here it was found convenient to combine the input from a horizontal and a vertical antenna in suitable proportions, in order to render the amplitudes of the ground and sky waves comparable.

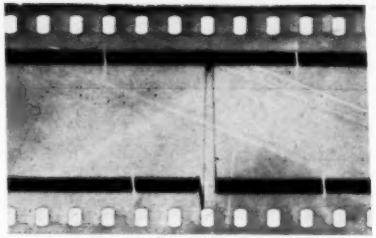
The group retardation method has the advantage that sky waves arriving from several paths of widely different retardations (or from several distinct layers) are readily and immediately resolved from the oscillograms, without the use of the more elaborate harmonic analysis required in the interpretation of results obtained by phase interference methods. (See fig. 1 (*b*).) This is of marked importance when multiple reflections and a large number of paths contribute to the results. (See fig. 5.) Investigations of this type have emphasized that, particularly during night conditions, the number of paths may be very great indeed and far from sharply defined.[7] Pulse methods may be used to investigate transmission on relatively low frequencies, down to perhaps 200 kc. per second. On lower frequencies, however, the length of the desired pulse begins to approach the period of the transmitted frequency and the time constant of the antenna. After this, difficulties introduced by transients and other obvious modulation limitations govern. The phase interference methods are, however, not free from difficulty at these lower frequencies, due to the large change of frequency required to produce the interference patterns. Under such conditions, a modification of the phase interference method, in which the path is varied instead of the frequency, is of

[4] See, for instance, E. V. Appleton, Proc. Royal Soc., vol. 109, p. 621; 1925; vol. 113, p. 450; 1926; vol. 115, p. 305; 1927; vol. 117, p. 576; 1929; vol. 126, p. 542; 1930; vol. 128, p. 134; 1930, vol. 128, p. 158; 1930. An application of a method essentially equivalent to the pulse method of Breit and Tuve has been recently described by T. L. Eckersley, Multiple Signals in Short Wave Transmission, Proc. I. R. E.; January, 1930.

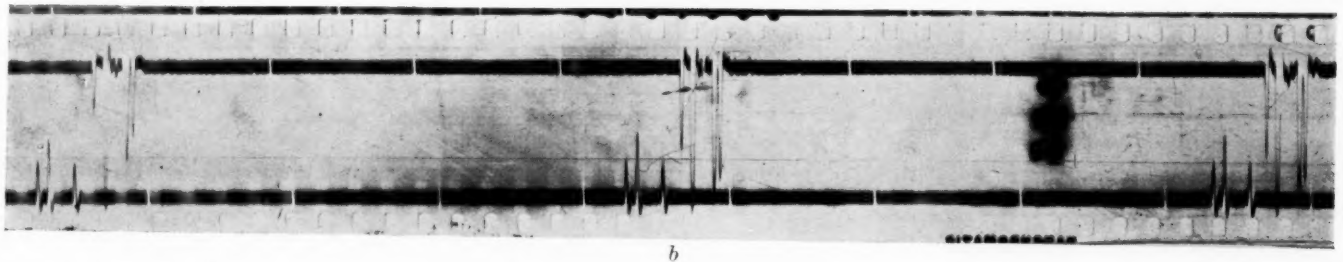
[5] E. V. Appleton, Proc. Physical Soc. (London), vol. 41, p. 43, 1928; also vol. 42, p. 321; June, 1930. Kenrick and Jen, Proc. I. R. E., vol 17, pp. 711–733; April, 1929.

[6] L. R. Hafstad and M. A. Tuve, An Echo Interference Method for the Study of Radio Wave Paths, Proc. I. R. E., vol. 17, pp. 1788–1792; October, 1929.

[7] de Mars, Gilliland, and Kenrick, Proc. I. R. E., vol. 19, pp. 106–113; January, 1931.



a



b

FIGURE 1.—*Types of oscillograms*

a, Type of pulse received in the absence of sky waves (interval between adjacent timing marks in all oscillograms shown is 1/120 second); *b*, lower trace shows pulse pattern received at 11.20 a. m., E. S. T., on August 16, 1930 (frequency 4,045 kc). Note strong peaks corresponding to 100 km and 330 km virtual heights in addition to ground wave peak Upper trace shows more complicated pattern at 11.24 a .m. Here we find strong peaks corresponding to virtual heights of 100, 290, and 330 km. Both traces read from left to right

particular interest.[8] The good accord obtained by the various methods, despite the difficulties peculiar to each, is encouraging. Some comparisons of this sort are included here.

In the work described here oscillographic records were made on frequencies ranging from 1,600 kc per second to 8,650 kc per second (including a number not previously observed).

The observations include the summer of 1930, which was one of marked magnetic disturbance. Observations during this period are hence of particular interest, although they can hardly be considered as typical summer conditions. Of particluar interest in this connection is the notable absence of multiple peaks on the higher frequencies during the summer months, although they were frequently observed on 8,650 kc during the winter and early spring. (See, for instance, the curves of Figure 2 where the average daytime virtual heights on 4,045 kc and 8,650 kc are indicated.) It should be pointed out that although the same transmitter was used on all of the frequencies during August and September, the radiated power was not measured and may have been enough less on the highest frequencies to indicate a cut-off frequency somewhat lower than that actually existing.

It will be noted that these curves show only predominant virtual heights. Diagrams are, however, also included, showing the observed virtual heights throughout the 24 hours on a number of frequencies. (See figs. 3, 4, 7, and 8.) Distinct evidence of the existence of two sharply defined regions corresponding to the E and F regions of Appleton, is also to be noted in a number of cases. An approximate analytical investigation of the effect of a lower layer on observed virtual heights from higher layers is also indicated.

II. 4045-kc OBSERVATIONS

Figure 2 presents graphs giving average daylight virtual heights on 4,045 and 8,650 kc, from January, 1930 to October, 1930. The observations from January to June were on transmission from the Naval Research Laboratory at Bellevue, Anacostia, D. C. These observations were interrupted when no transmitting facilities were available at the Naval Research Laboratory for this purpose during the summer of 1930. However, during the early summer a transmitter was placed in operation at the National Bureau of Standards experimental station near Alexandria, Va., which permitted the observations described to be made during August and September. All oscillograms of the received signals were recorded at the National Bureau of Standards experimental station at Kensington, Md. The distance from the transmitter to receiver was, in each case, about 20 km.

It will be noted by reference to Figure 2 that on 8,650 kc only single pulses were received, except for the period from February 6 to April 7 when multiple patterns were obtained. A rise in virtual height on 4,045 kc followed the disappearance of the multiple patterns on 8,650 kc. It will be noted that this high virtual height persisted during the summer with temporary fluctuations to lower values, but in all

[8] J. Hollingworth, The Propagation of Radio Waves, J. I. E. E., (London) pp. 579-595; May, 1926. A recent interesting application of this method has also been reported on much higher frequencies. See C. B. Mirick and E. R. Hentschel, Proc. I. R. E., vol. 17, pp. 1034-1041; June, 1929. At the higher frequencies a rapidly moving recording system is essential to this method due to frequent inadvertent path changes during the observations from other causes, such as layer movements, etc.

cases the pattern on 8,650 kc remained single during the period of observations reported.

In addition to the very high values of the virtual height of the *F* layer, distinct evidence of the existence of the *E* layer on 4,045 kc during the daytime was to be found on numerous occasions during the middle of August. (Fig. 3.) Figure 1(*b*) gives an oscillograph trace showing this phenomenon, and scatter diagrams contrasting this effect with conditions a few days later are shown in Figure 4. The actual values of virtual heights as read from the records are plotted as points, the lowest distinct height from each record being indicated by a cross, and distinct greater heights (not in simple multiple relation) are denoted by dots. The marked frequency with which the

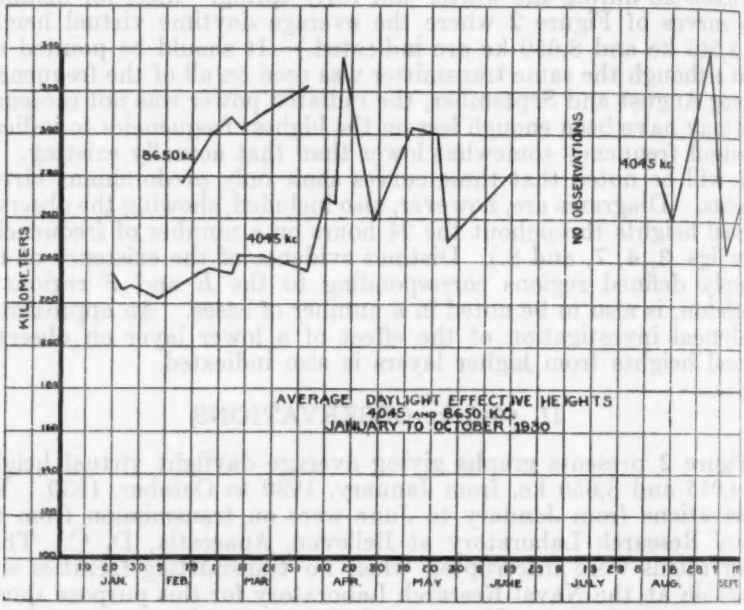


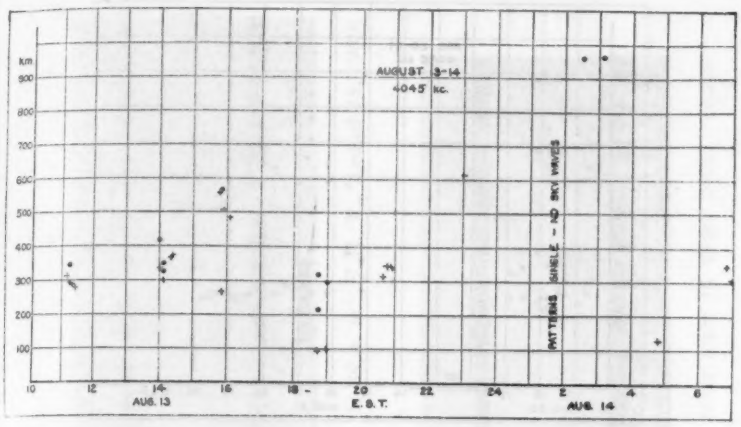
FIGURE 2.—*Average daylight (virtual) heights of the Kennelly-Heaviside layer from January to October, 1930 (4,045 and 8,650 kc)*

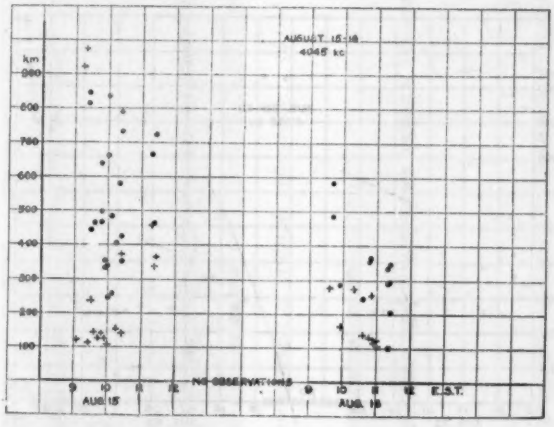
Note sky waves returned on 8,650 kc only between February and April of the period of observations.

100 km layer was observed during the daytime on 4,045 kc on August 15 and 16 (fig. 3) is, it will be noted, in marked contrast to the phenomena observable a few days later (August 20 and 21). (Fig. 4.) An interesting phenomenon in the form of a progressive downward movement of virtual height on 4,045 kc during the afternoon observed on August 25 and also on August 26, is also shown in Figure 4. This is one of the few cases where heights between 150 and 200 km were observable (that is, heights intermediate between the frequently occurring 100 to 130 and 250 to 300 km virtual heights referred to as the *E* and *F* regions or layers. [4] The pronounced low layer is clearly shown in the oscillogram of Figure 5, and the presence of a strong peak giving a high virtual height is shown in Figure 6.

The persistent appearance of large virtual heights not readily explicable on the basis of simple multiple reflections from the *E* or *F*

[4] See footnote 4, p. 1084.





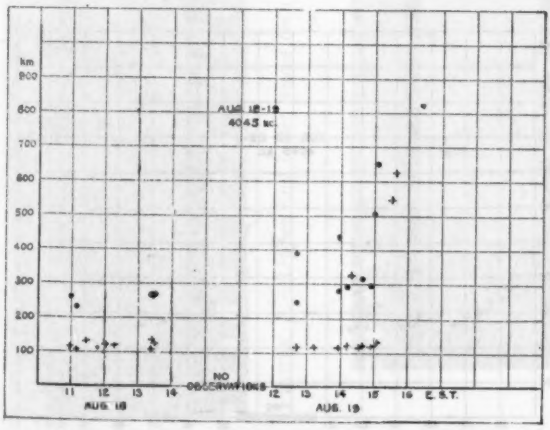


FIGURE 3.—*Scatter diagram of virtual heights observed during the period extending from August 13 to August 19, 1930*

Note frequent occurrence of 100 km heights.

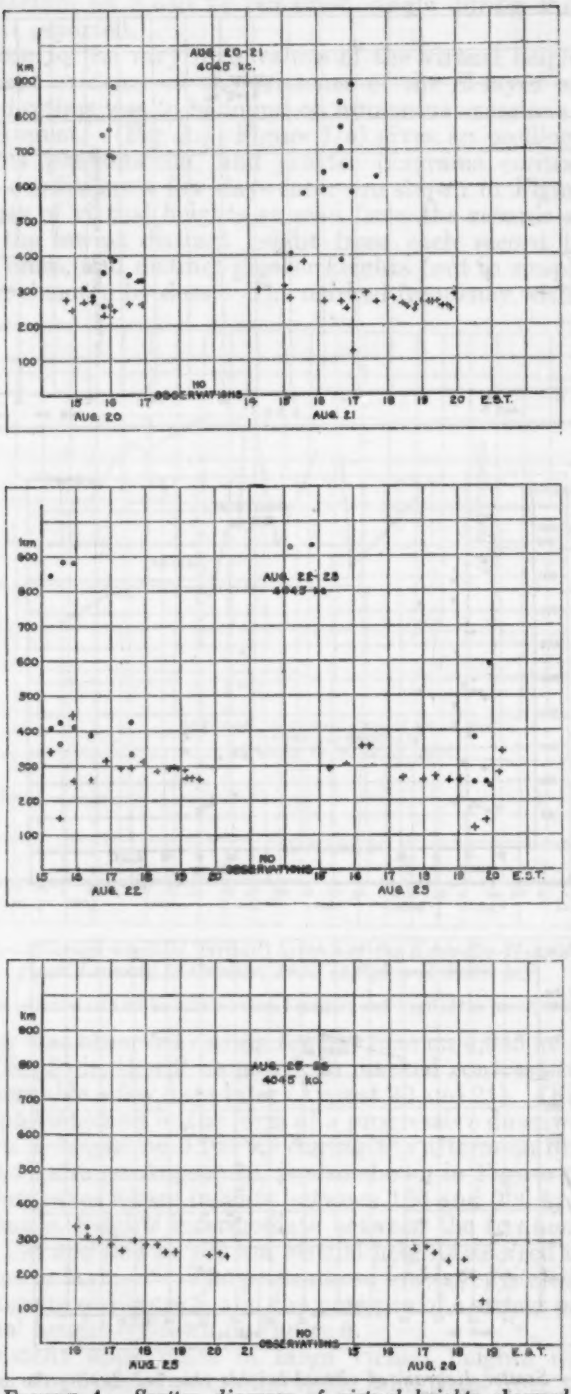


FIGURE 4.—*Scatter diagram of virtual heights observed during the period extending from August 20 to August 26, 1930* Note rare occurrence of 100 km heights.

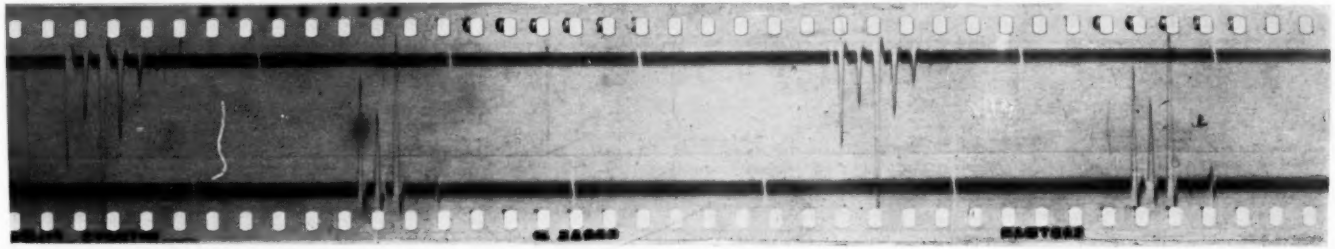


FIGURE 5.—*Upper and lower traces both show example of multiple reflections. (4,045 kc, 11.30 a. m., E. S. T., August 18, 1930)*

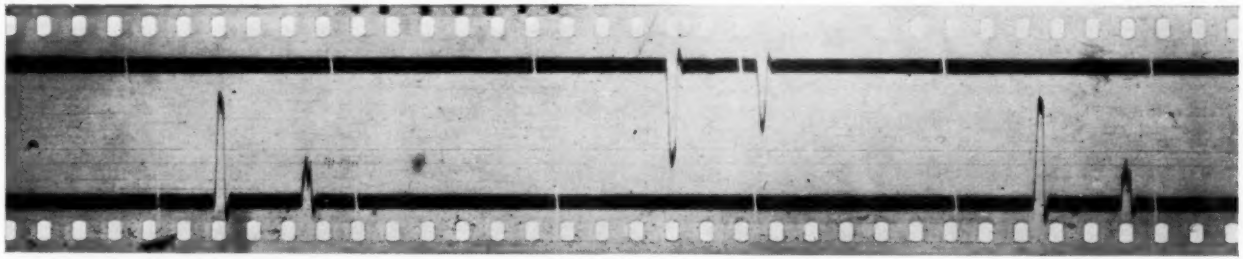


FIGURE 6.—*Note predominant 565 km virtual height. Note, however, faint evidence lower layer in upper trace. (4,045 kc, 3.50 p. m., E. S. T., August 13, 1930)*

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layers, is emphasized in many of the oscillograms. (See, for instance, figs. 1(*b*) and 6.) Phenomena of this nature must doubtless be taken into account as the theory develops, for these phenomena are apparently quite typical. A possible explanation is suggested by the theory presented in this paper.

III. VIRTUAL LAYER HEIGHTS AS A FUNCTION OF FREQUENCY DURING DAYTIME

During August and September frequent observations were made on 1,600, 2,000, 3,000, 4,045, 5,000, 6,425, and 8,650 kc, approximately the same number of observations being taken on each frequency. The results obtained during daytime (9 to 15 e. s. t.) are shown in Figure 7. No reflections were observed on 6,425 and 8,650 kc during

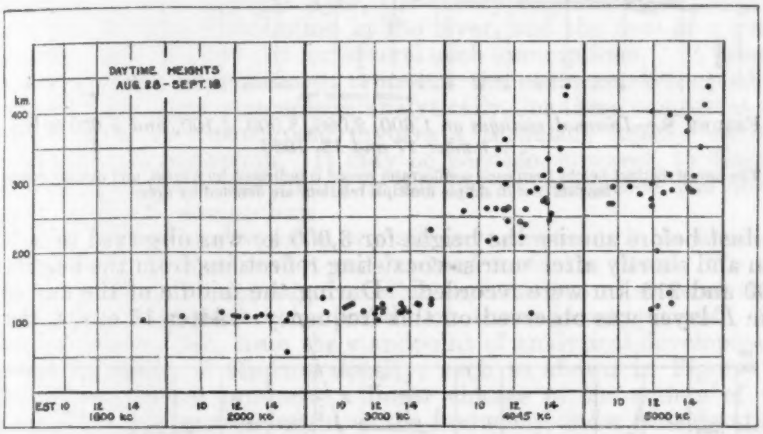

FIGURE 7.—*Daytime heights observed for 1,600, 2,000 3,000, 4,045, and 5,000 kc between August 28 and September 18, 930*

these hours. This is in marked contrast to the conditions between February to April, when multiple reflections on 8,650 kc were frequently observed.

The patterns obtained for many of the observations, even on the lower frequencies, showed only the ground wave. Figure 7 indicates the number of times that reflections occurred on the various frequencies. It will be noted that virtual heights between 100 and 150 km, corresponding to the *E* layer, appear for 1,600, 2,000, and 3,000 kc. Occasionally this layer was observed on 4,045 and 5,000 kc, but virtual heights of over 200 km occurred most frequently on these higher frequencies. Once on 3,000 kc and twice on 5,000 kc, coexisting *E* and *F* layers were observed. Only the first, or in case of coexisting *E* and *F* layers, the first two reflections, were plotted in Figure 7.

IV. DIURNAL VARIATION

Figure 8 shows the results obtained for frequencies of 1,600, 2,000, 3,000, 4,100, and 5,000 kc for a 24-hour period (September 17 to 18). The *E* layer was observed on 1,600 kc shortly after sunrise and just before sunset. Otherwise no reflections were observed on this fre-

quency during daylight. However, just after sunset the virtual height was observed to be 232 km and during the night the height increased to 300 km. At sunrise it again dropped to the *E* layer region.

On 2,000 kc reflections were observable only three times during the 24 hours and the heights corresponded closely to those for 1,600 kc.

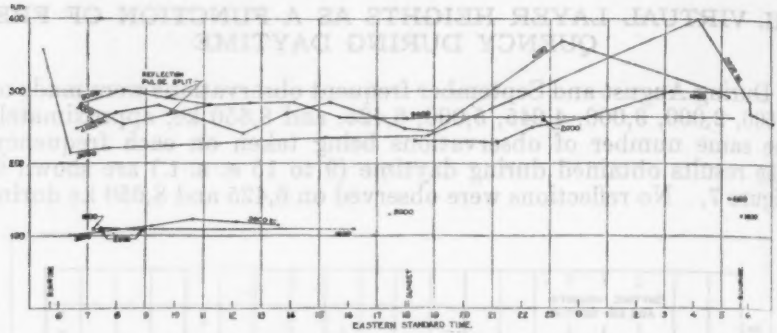

FIGURE 8.—*Diurnal changes on 1,600, 2,000, 3,000, 4,100, and 5,000 kc September 17 and 18, 1930*

The lowest distinct height from each oscillograph record is indicated by a cross, and distinct greater heights (not in simple multiple relation) are denoted by dots.

Just before sunrise the height for 3,000 kc was observed to be 357 km and shortly after sunrise coexisting reflections from the heights of 100 and 215 km were recorded. During the middle of the day only the *E* layer was observed on this frequency. After 15 e. s. t. the *E*

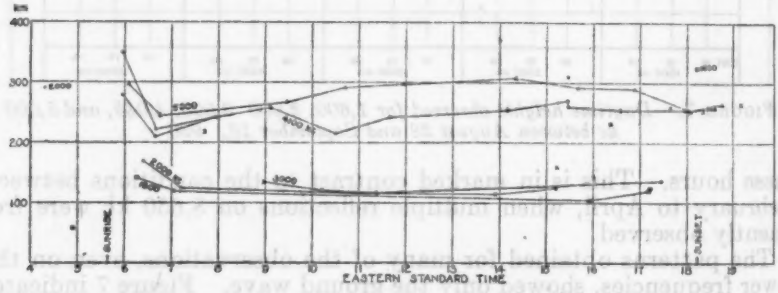

FIGURE 9.—*Diurnal changes on 1,600, 2,000, 3,000, 4,100, and 5,000 kc September 12, 1930*

The lowest distinct height from each oscillograph record is indicated by a cross, and distinct greater heights (not in simple multiple relation) are denoted by dots.

layer was no longer observable but reflections from the *F* region were again noted.

The behavior on 4,100 and 5,000 kc is clearly shown on the diagram. It will be noted that on 4,100 kc coexisting reflections from heights of 153 and 295 km were observed shortly before sunrise on the 18th.

Figure 9 shows diurnal variations for the same frequencies for a slightly shorter period on September 12.

V. ANALYTICAL DISCUSSION OF RESULTS

1. REFRACTION

The phenomena observed in these tests offer evidence in favor of the existence of at least two more or less sharply defined strata in the upper atmosphere at which refraction takes place (as already suggested by other investigations conducted previously).[9,10] The refraction theory for one layer has already been discussed,[11,12] but it is of interest to consider the relations when two well-defined ionized strata exist. As Appleton has suggested, rays which are finally returned from the upper stratum nevertheless give virtual heights which may be considerably altered due to the transit through the lower layer. It is of interest to consider this possibility analytically to determine if such a view is in accord with observed phenomena. As in the case of a single layer, the theory requires an assumption as to the electron distribution in the layer, and the case of a single layer has been worked out for several such assumptions. At present it is, of course, impossible to represent the exact conditions which obtain in the upper atmosphere analytically, for these conditions are very imperfectly known and involve a turbulent rapidly varying distribution of ionization. It may be possible, however, to disclose some of the salient phenomena on the basis of simplified and necessarily idealized assumptions.

In the following discussion we will investigate such an idealized treatment to determine if it can be used to fit the facts. We will also investigate certain other possible explanations of some of these phenomena suggested as a result of those investigations. The simplest assumption, from the standpoint of analytical development, is a distribution of electron density, such as shown in Figure 10; that is, one which produces a linear change of the square of the index of refraction with height at the frequency under consideration. Under such conditions the path is (in the case of a single layer) parabolic. Several other assumed variations of electron density giving other types of trajectories have been investigated[13] and shown to yield rather similar results in the single layer case, provided the curves do not have a minimum index of refraction near zero. Under such conditions long retardations may be encountered.[14] These distributions, however, represent critical border line conditions and will not be considered here. In view of the above considerations, and with due regard to the simplicity attainable, the linear variation of squared index of refraction of the form shown in Figure 10 has been selected.

The postulated distribution considers a linear decrease in the square of the index of refraction starting at a height E_0 and decreasing linearly to a value m^2 at a height E_1.

The square of the index of refraction is then assumed to remain constant at the value m^2 until a height F_0 is reached, when it again starts to decrease linearly to a value zero at a height F_1.

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[9] See footnote 4, p. 1084.
[10] See footnote 7, p. 1034.
[11] See footnote 5, p. 1084.
[12] P. O. Pedersen, The Propagation of Radio Waves, published by Denmarks Naturvioenkabeliage Samfund, Copenhagen; 1928.
[13] See footnote 5, p. 1084.
[14] G. Breit, Group Velocity and Retardation of Echoes, Proc. I. R. E., vol. 17, pp. 1508-1512; September, 1929.

The layers are suggested schematically in Figure 11 where the equations corresponding to the assumed linear deviations are also indicated. A curve showing the trajectory and indicating the nota-

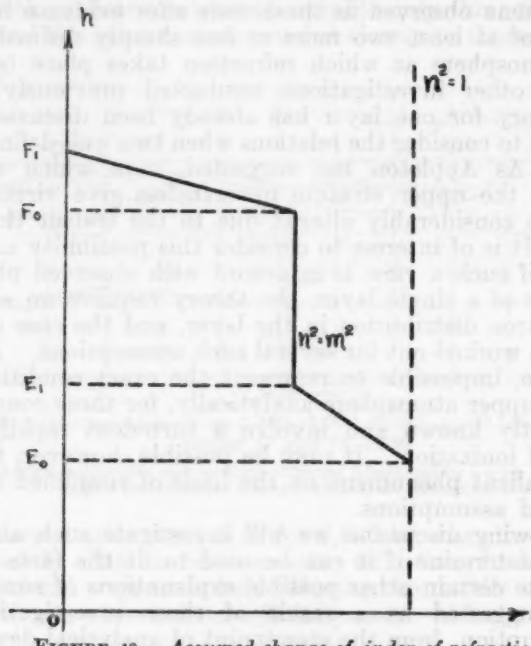

FIGURE 10.—*Assumed change of index of refraction squared as a function of height*

tion adopted is given in Figure 12. In carrying out the computations of virtual height for this case, free use will be made of the notation and the results evolved in a previous paper.[15]

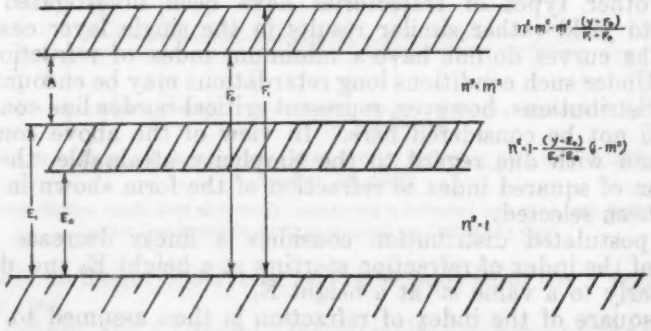

FIGURE 11.—*Assumed layer distribution showing equations for variation of n*

In computing the virtual height h' we will avail ourselves of Breit and Tuve's theorem (1) which tells us that in the absence of dissipation (for any assumed variation of index of refraction with height),

[15] See equation (V–1), p. 720, Kenrick and Jen, Measurement of the Height of the Kennelly-Heaviside Layer, Proc. I. R. E., vol 17, pp. 711–733; April, 1929.

the group retardation is the same as that encountered by a ray traveling with the velocity of light, and traversing a triangular path with the given base and given angle of departure. Hence (see fig. 12 for notation),

$$X_0 = 2\,h' \tan \phi_0 \tag{1}$$

This gives us a relation between the virtual height h', the angle of departure ϕ_0, and the base X_0.

We will now compute the relation between the coordinate $\frac{X_0}{2}$ and ϕ_0 by adding together the x intervals corresponding to each part of the path. This will enable us to compute the relation between actual height of the strata, the virtual height, m, ϕ_0, etc.

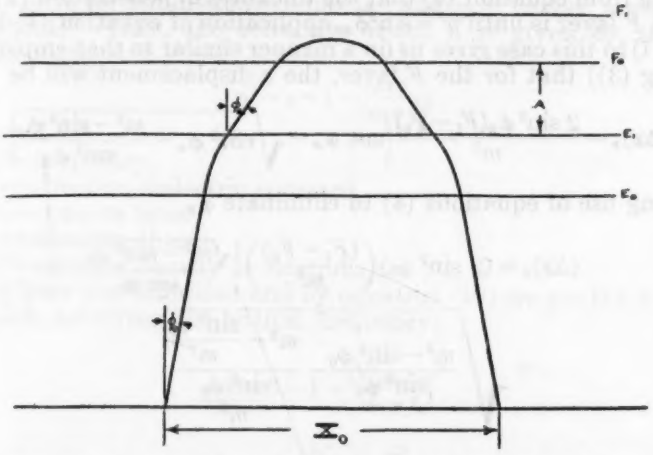

FIGURE 12.—*Form of trajectory of ray in presence of two layers*

The ray moves in a straight line as far as the height E_0; hence its horizontal displacement thus far is merely

$$(\Delta x)_{z_0} = E_0 \tan \phi_0 \tag{2}$$

The ray travels in a parabolic arc through the E layer. Its horizontal displacement during this part of its motion is [16]

$$(\Delta x)_{z_1 - z_0} = \frac{2 \sin^2 \phi_0}{1 - m^2} (E_1 - E_0) \left\{ \cot \phi_0 - \sqrt{\cot^2 \phi_0 - \frac{(1 - m^2)}{\sin^2 \phi_0}} \right\} \tag{3a}$$

or

$$(\Delta x)_{z_1 - z_0} = \frac{2 \sin \phi_0 \cos \phi_0}{1 - m^2} (E_1 - E_0) \left(1 - \sqrt{1 - \frac{1 - m^2}{\cos^2 \phi_0}} \right) \tag{3b}$$

The ray leaves the E layer at angle given by the Snell law and the differential equation of the ray path (see reference 11; Equation III–1); that is

$$\sin \phi_s = \frac{\sin \phi_0}{m} \tag{4a}$$

[16] See footnote 14, p. 1091.

from equation (4a) we have, by elementary trigonometry, that

$$\cos \phi_E = \frac{\sqrt{m^2 - \sin^2 \phi_0}}{m} \tag{4b}$$

and hence

$$\tan \phi_E = \frac{\sin \phi_0}{\sqrt{m^2 - \sin^2 \phi_0}} \tag{4c}$$

Using equations (4a) and (4c), and denoting the distance between the layers $(F_0 - E_1)$ by A, we have immediately that the x displacement of the ray in passing from E_1 to F_0 is:

$$(\Delta x)_{F_0 - E_1} = (F_0 - E_1) \tan \phi_E = \frac{(A) \sin \phi_0}{\sqrt{m^2 - \sin^2 \phi_0}} \tag{5}$$

Noting from equation (4) that the thickness of penetration $(Y_F - F_0)$ into the F layer is until $n^2 = \sin^2 \phi_E$, application of equation (V–1a, reference 11) to this case gives us (in a manner similar to that employed in deducing (3)) that for the F layer, the x displacement will be

$$(\Delta x)_F = \frac{2 \sin^2 \phi_E (F_1 - F_0)}{m^2} \left\{ \cot \phi_E - \sqrt{\cot^2 \phi_E - \frac{m^2 - \sin^2 \phi_E}{\sin^2 \phi_E}} \right\} \tag{6a}$$

or making use of equations (4) to eiliminate ϕ_E

$$(\Delta x)_F = (2 \sin^2 \phi_0) \left(\frac{(F_1 - F_0)}{m^2} \right) \left\{ \frac{\sqrt{m^2 - \sin^2 \phi_0}}{\sin \phi_0} - \sqrt{\frac{m^2 - \sin^2 \phi_0}{\sin^2 \phi_0} - \frac{m^2 - \dfrac{\sin^2 \phi_0}{m^2}}{\dfrac{\sin^2 \phi_0}{m^2}}} \right\} \tag{6b}$$

or

$$(\Delta x)_F = \frac{2 \sin \phi_0 \, (F_1 - F_0) \, (\sqrt{m^2 - \sin^2 \phi_0})}{m^4} [1 - \sqrt{1 - m^2}] \tag{6c}$$

Adding together equations (2), (3b), (5), and (6) to obtain the total $\frac{x_0}{2}$ (and utilizing equation (1) involving the virtual height,) we have:

$$\frac{x_0}{2} = h' \tan \phi_0 = E_0 \tan \phi_0 + (2 \sin \phi_0 \cos \phi_0) \frac{E_1 - E_0}{1 - m^2} \left(1 - \sqrt{1 - \frac{1 - m^2}{\cos^2 \phi_0}} \right)$$
$$+ A \frac{\sin \phi_0}{\sqrt{m^2 - \sin^2 \phi_0}} + \frac{2 \sin \phi_0 (F_1 - F_0) \sqrt{m^2 - \sin^2 \phi_0}}{m^4} [1 - \sqrt{1 - m^2}] \tag{7a}$$

Hence

$$h' = E_0 + 2 \cos^2 \phi_0 \left(1 - \sqrt{1 - \frac{1 - m^2}{\cos^2 \phi_0}} \right) \frac{E_1 - E_0}{1 - m^2} + \frac{A \cos \phi_0}{\sqrt{m^2 - \sin^2 \phi_0}}$$
$$+ \frac{2 (F_1 - F_0) \cos^2 \phi_0 \sqrt{m^2 - \sin^2 \phi_0} \, [1 - \sqrt{1 - m^2}]}{m^4} \tag{8}$$

So far, no approximations have been made, and equation (8) may be used to solve for h' for any x (by successive approximations).

However, when X_0 is small; that is, when we are working at nearly normal incidence, and when m^2 is small with respect to unity but large with respect to $\sin^2\phi_0$, equation (8) may be written approximately as

$$h' = E_0 + \frac{2(E_1 - E_0)}{1+m} + \frac{A}{m} + \frac{F_1 - F_0}{m} \tag{9a}$$

If now we define the critical frequency as that frequency for which the index of refraction of the E layer is zero, then for slightly higher frequencies m will be small and the effective distance between layers may be increased to several times its actual value as may be seen from equation (9a). This effect, then, offers a possible explanation for the erratic heights observed for the F layer.

The relation between m and frequency may be written in a convenient form for nondissipative media (which, of course, are assumed throughout). Thus, the refractive index n is given by the well-known equation:[17]

$$n^2 = \epsilon = 1 - \frac{Ne^2}{m_1 \pi f^2} \tag{10}$$

where

f = frequency,
ϵ = effective dielectric constant,
m_1 = electron mass,
e = electron charge,
N = electron density in electrons/cc.

Thus from our definition and by equation (10) we get the following expression involving the critical frequency:

$$n^2 \equiv 0 = 1 - \frac{N_{(\max)E} e^2}{m_1 \pi f_c^2} \tag{11a}$$

or

$$f_c^2 = \frac{N_{(\max)E} e^2}{m_1 \pi} \tag{11b}$$

where $N_{(\max)E}$ is the maximum electron density of the E layer. f_c is the highest frequency for which energy is returned by refraction at normal incidence from a nonturbulent layer of the type assumed in this analytical investigation.

On substituting f_c^2 for $\frac{N_{(\max)E} e^2}{m_1 \pi}$ in equation (10) the square of the index of refraction at the highest point of the E layer is given by:

$$m^2 \equiv n^2_{(\min)E} = 1 - \left(\frac{f_c}{f}\right)^2 \tag{11c}$$

If for a particular time we take $f_c = 3{,}750$ kc, then at 4,000 kc, $m = \sqrt{1 - \left(\frac{3.75}{4}\right)^2} = 0.35$ and the distance between layers indicated by height measurements would be about three times too great. Thus this critical value indicates an explanation for the virtual heights of 500 km or more, which were frequently observed during the tests.

[17] See footnote 12, p. 1091.

The critical frequency, which is proportional to the square root of the electron density, is extremely variable, and doubtless changes considerably from hour to hour.

The theory developed above would permit the coexistence of E and F layer reflections only very near the critical frequency. Thus just below the critical frequency no energy will get through the E layer for a given angle of incidence and a reflection from this layer will occur. However, at a slightly smaller angle of incidence energy can get through the E layer and be reflected from the F layer. During the tests described such coexisting reflections were observed at various times on 3,000, 4,100 and 5,000 kc, so that the value of f_c chosen may be considered as a fair example for calculating the maxi-

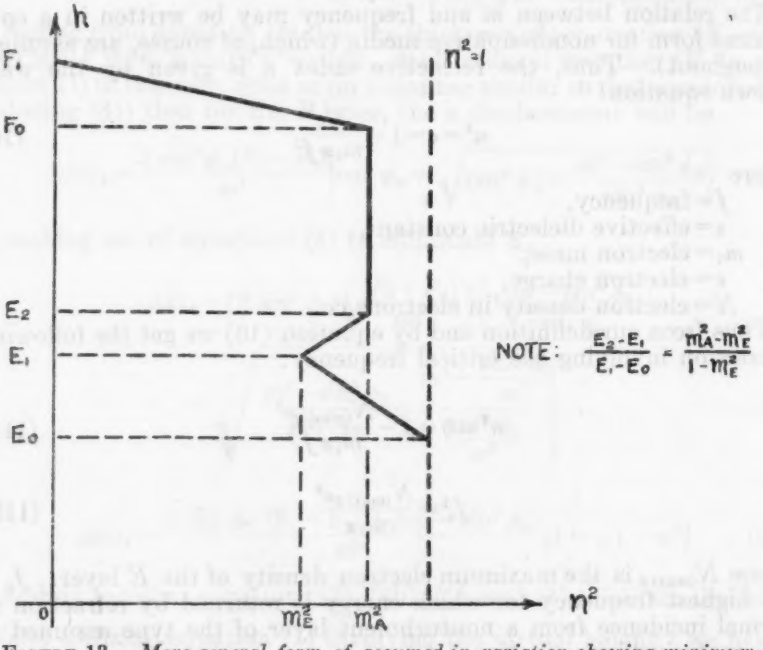

FIGURE 13.—*More general form of assumed in variation showing minimum value in first layer*

mum electron density in the E layer by means of equation (11b). This calculation gives

$$N_{MAX}\ (E \text{ layer}) = 1.7 \times 10^5 \text{ electrons per cc.}$$

A similar computation for the summer F layer, assuming value $f_c = 5{,}500$ kc, gives

$$N_{MAX}\ (F \text{ layer}) = 3.8 \times 10^5 \text{ electrons per cc.}$$

Little specific information is available as to the electron distribution in the upper atmosphere, but it is perhaps appropriate to consider a slight generalization of the above analysis, for, thus far, it will be noted we have considered the reduction of n^2 with height to be progressive; that is, no maximum and subsequent minimum of

N was considered between the layers. A more general type of variation to which the above analysis may be readily extended is obtained by an assumption such as indicated in Figure 13.

This variation differs from that of Figure 10 only in that the n^2 variation is assumed to reach a minimum $m^2{}_E$ in the E layer and then n^2 is again assumed to increase (along a symmetrical straight line of equal slope) to a value $m^2{}_A$, where it remains until the height F_0 is attained. The equation of the variations are indicated in Figure 14, and the generalization of equation (7) to include this case gives

$$\frac{x_0}{2}=h' \tan \phi_0 = E_0 \tan \phi_0 + 2\left[2 \sin \phi_0 \cos \phi_0 \frac{E_1-E_0}{1-m^2{}_E}\left(1-\sqrt{1-\frac{1-m^2{}_E}{\cos^2\phi_0}}\right)\right]$$

$$-2 \sin \phi_0 \cos \phi_0 \frac{(E_1-E_0)}{1-m^2{}_E}\left(1-\sqrt{1-\frac{1-m^2{}_A}{\cos^2\phi_0}}\right)+\frac{[A-(E_2-E_1)] \sin\phi_0}{\sqrt{m^2{}_A-\sin^2\phi_0}}$$

$$+2 \sin \phi_0 \frac{(F-F_0)\sqrt{m_A{}^2-\sin^2\phi_0}}{m_A{}^4}\left[1-\sqrt{1-m_A{}^2}\right]$$

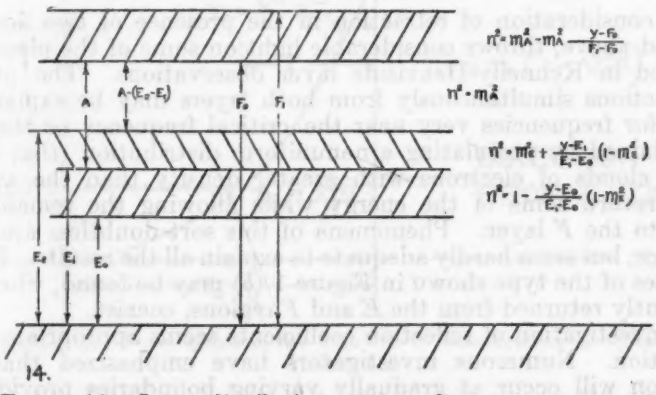

FIGURE 14.—*Layer distribution corresponding to more general variation of n indicated in Figure 13*

In writing this equation we note that, for this case, by symmetry, the parabolic path $(\Delta x)E_0-E_2$ would be just twice its value in equation (7a) provided $m_A{}^2=1$. For general variations corresponding to other values of $m^2{}_A$, $(\Delta x)E_0-E_2$ is twice that of equation (7a) minus the (Δx) corresponding to the change from $n^2=1$ to $n^2=m_A{}^2$ along the parabolic path; this is represented by the subtractive term of equation (7b).

The approximations previously employed in deducing equation (9) from equation (7) may be applied (subject to the same approximations) to deduce from equation (13) the value of virtual heights h' for the generalized case, that is,

$$h'=E_0+\frac{2(E_1-E_0)}{1-m_E{}^2}(1-2m_E+m_A)+\frac{A-(E_2-E_1)}{m_A}+\frac{F_1-F_0}{m_A} \quad (9b)$$

It will be noted that when $m_A=m_E$ and $(E_2-E_1)=0$, equations (7b) and (9b) reduce, respectively, to (7a) and (9a).

The nature of the phenomena indicated by equations (7b) and (9b) is not essentially different from that previously discussed, but indicates that for a given $F_1 - E_0$ and m_s the variation in virtual height of the F layer produced by the E layer is greatest when the maximum m_4^2 between the layers is small (that is, when there is no pronounced decrease in N between the layers). The values indicated in the discussion of equation (9) are thus upper bounds (at least for the types of variations assumed). Previous investigations have indicated the conclusions to be independent of the exact form of variations assumed,[18] except for certain very special conditions,[19] and the relations deduced above may hence be considered as reasonably representative. In general, we would expect the value of m_4 to be distinctly less than unity, so the phenomena discussed will be in evidence, in general, near the critical frequency for the E layer. (Note that if m_4 is not considerably less than unity, equation (7b) should be used, as equation (9b) is no longer a good approximation).

2. REFLECTION PHENOMENA

The consideration of refraction in the presence of two layers, as outlined above, throws considerable light on some of the phenomena observed in Kennelly-Heaviside layer observations. The presence of reflections simultaneously from both layers may be explained as above for frequencies very near the critical frequency or they may be explained by postulating a nonuniform distribution (that is, turbulent clouds of electrons with greater density than the average) which return some of the energy while allowing the remainder to travel to the F layer. Phenomena of this sort doubtless are of importance, but seem hardly adequate to explain all the results. Numerous cases of the type shown in Figure 1 (*b*) may be found, where rays apparently returned from the E and F regions, coexist.

An investigation of reflection coefficients seems appropriate in this connection. Numerous investigators have emphasized that little reflection will occur at gradually varying boundaries provided the first and second derivatives of the variation are not large and do not exhibit discontinuities, in short, provided the variation extends over a number of wave lengths and is free from abrupt stratifications.[20] [21] [22]

It must be remembered, however, that the power returned, is usually small and so variable that reflection coefficients of a few per cent would be sufficient to explain many of the observed phenomena. It therefore seemed appropriate to review quantitatively the reflection theory with a view to establishing how much this phenomenon might be invoked to explain the results. In this paper we will confine ourselves for simplicity to the case corresponding to most of the observations; that is, that of normal incidence.

Lord Rayleigh's work is notable among the investigations of this problem of the reflection at normal incidence from gradually varying media. He obtained solutions directly from the differential equation of the motion (for certain special assumed laws of variations of the medium which rendered the resulting equation integrable).[21] He

[18] See footnote 5, p. 1084.
[19] See footnote 14, p. 1091.
[20] See footnote 12, p. 1091.
[21] Rayleigh (Strutt, J. W.), On Reflection of Vibrations at the Confines of Two Media Between Which the Transition is Gradual, Proc. London Math. Soc., pp. 51–56; 1881.
[22] Rayleigh (Strutt, J. W.), On the Propagation of Waves Through a Stratified Medium with Special Reference to the Question of Reflection. Collected Works, vol 6, pp. 71–90.

also obtained the solution as a limiting case of the solution for stratified transitions as the number of stratifications became infinite and the amplitude of the transitions between any two strata infinitesimal.[23]

The most general (and for our purposes, the most convenient) relation he derives is to be found in the second paper. (See ref. 22, p. 80, equation (5).) Rayleigh's investigations are not limited to waves in optical media, but, as he points out, may be readily reduced

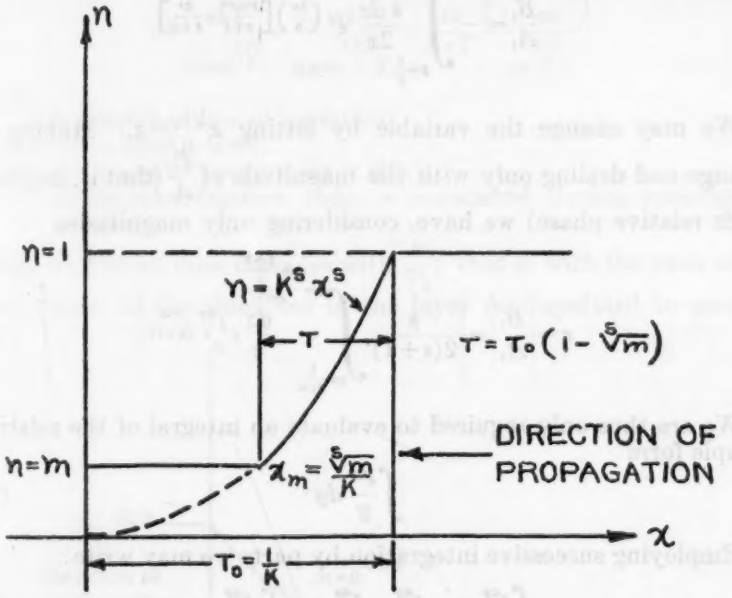

FIGURE 15.—*Form of transition assumed in investigation of reflection. (Case I)*

to this case. When so reduced, this equation may be written in our notation as:

$$\frac{B_1}{A_1} = -\int \frac{dn}{2n} \varepsilon^{-2j\int_0^x \frac{2\pi n}{\lambda n_0} dx} \tag{12}$$

where

n = index of refraction at any point x in the variable medium.
λ = wave length in vacuo.
$j = \sqrt{-1}$
B_1 = amplitude of reflected wave.
A_1 = amplitude of incident wave.
r = reflection coefficient at normal incidence.

It should be noted that $\left|\frac{B_1}{A_1}\right| = r$. This relation will be used in this investigation.

The results, of course, depend on the assumed type of variation of dielectric constant, but an idea of the magnitude to be expected may be obtained by investigating some plausible distributions.

We will now proceed to evaluate equation (12) for rather general types of variation of n with x.

[23] See footnote 22 p. 1098.

Case I.—We will first consider a variation of the form $n=k^s x^s$. (See fig. 15.)

Substituting this value of n in equation (12) we have for the reflection (for a strata varying from an $n=1$ to an $n=m$ along the assumed curve)

$$\frac{B_1}{A_1}=-\int_{x=\frac{1}{k}}^{x=\sqrt[s]{\frac{m}{k}}}\frac{s\,dx}{2x}\,\epsilon^{j\left(\frac{4\pi}{\lambda}\right)\left[\frac{k^{s+1}x^{s+1}}{s+1}-\frac{k^s}{s+1}\right]} \tag{13}$$

We may change the variable by letting $x^{s+1}=z$. Making this change and dealing only with the magnitude of $\frac{B_1}{A_1}$ (that is, neglecting their relative phase) we have, considering only magnitudes

$$r=\left|\frac{B_1}{A_1}\right|=\left|\frac{s}{2(s+1)}\int_{z=\frac{1}{k^{s+1}}}^{z=m^{\frac{s+1}{s}}k^{s+1}}\frac{dz}{z}\,\epsilon^{j\frac{4\pi}{\lambda}\frac{k^s z}{(s+1)}}\right| \tag{14}$$

We are thus only required to evaluate an integral of the relatively simple form

$$\int\frac{\epsilon^{ay}}{y}\,dy \tag{15a}$$

Employing successive integration by parts we may write:

$$\int\frac{\epsilon^{ay}}{y}\,dy=\frac{\epsilon^{ay}}{ay}+\frac{\epsilon^{ay}}{a^2y^2}+2\int\frac{\epsilon^{ay}}{a^2y^3}\,dy \tag{15b}$$

For real values of y and pure imaginary values of a this series may be written in the asymptotic form:

$$\left|\int\frac{\epsilon^{ay}}{y}\,dy\right|=\left|\frac{\epsilon^{ay}}{ay}+\frac{\epsilon^{ay}}{a^2y^2}\right|+2R\int\frac{dy}{a^2y^3}\qquad -1\leqq R\leqq 1 \tag{15c}$$

Remembering that a is a pure imaginary, we note that the integral in general represents a rapidly pulsating function but that always

$$\left|\int\frac{\epsilon^{ay}}{y}\,dy\right|\leqq\left|\frac{1}{ay}\right|+\left|\frac{1}{a^2y^2}\right|+\left|\frac{1}{a^2y^3}\right| \tag{15d}$$

Applying (15d) to integral 14, and further approximating by neglecting phase differences at the limits, we may write further the order of magnitude of $\left(\frac{B_1}{A_1}\right)$ by the inequality

$$r=\left|\frac{B_1}{A_1}\right|\leqq\frac{s}{2(s+1)}\left\{\left|\frac{(s+1)k\lambda}{4\pi}\left(\frac{1}{m^{\frac{s+1}{s}}}+1\right)\right|+2\,\frac{(s+1)^2k^2\lambda^2}{16\pi^2}\left(\frac{1}{m^{\frac{2(s+1)}{s}}}+1\right)\right\} \tag{16}$$

For $\frac{1}{m}$ large compared with unity and $\frac{(s+1)\lambda k}{4\pi m^{\frac{s+1}{s}}}$ small compared with unity, this inequality approaches an equality to terms of the order of r^2, the function ceases to oscillate violently, and we may write (noting further that $\frac{T}{T_0}=\left(1-m^{\frac{1}{s}}\right)$

$$r \doteq \frac{sk\lambda}{8\pi m^{\frac{s+1}{s}}} = \frac{s\lambda}{8\pi m^{\frac{s+1}{s}} T_0} = \frac{s\lambda}{8\pi T} \frac{\left(1-m^{\frac{1}{s}}\right)}{m^{\frac{s+1}{s}}} \tag{17}$$

where

s = exponent of law of variation.
λ = wave length (km).
T = thickness of varying layer (km).
m = minimum refractive index n encounted during variation in layer.

This coefficient does decrease with $\frac{\lambda}{T_0}$; that is, with the ratio of the wave length to the thickness of the layer (extrapolated to zero n),

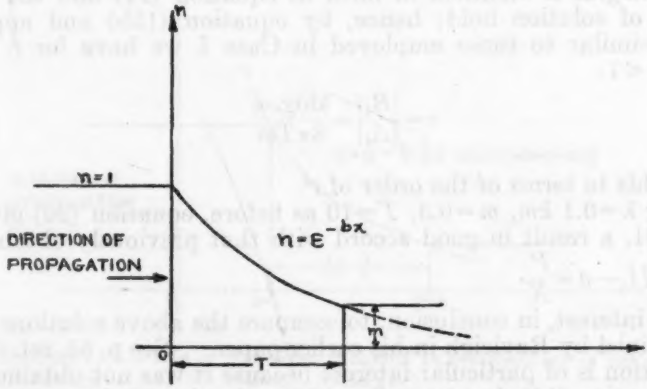

FIGURE 16.—*Form of transition assumed in investigation of reflection (Case II)*

but it will be noted the decrease is only linear; that is, for small coefficients of reflection the coefficient r is inversely proportional to the first power of the thickness of the layer. This coefficient varies (but not critically) with the powers of the variation of n with x. Thus, for a linear variation ($s=1$) we have, taking $T=10$ km, $\lambda=0.1$ km, and $m=0.3$; $\frac{s(1-m)}{8\pi(m^2)}=0.3$ and $r=0.003$. For $s=2$, the other data remaining the same, we have $\frac{s(1-m^{\frac{1}{2}})}{8\pi(m^{\frac{1}{2}})}=0.2$ and $r=0.002$; likewise for $s=3$, $r=0.002$.

While these coefficients of reflection are small, they are nevertheless quite appreciable, and reflections thus produced should be quite observable. It will be noticed further that close to the critical frequency much larger values of r may be found due to the small values of n encountered in that region. (However, note that the equation for r is, of course, not valid unless $r^3 << r$.)

Case II.—$n=\epsilon^{-bx}$. We will next consider an assumed variation of the form $n=\epsilon^{-bx}$.

As will be noted by reference to Figure 16, we will consider an exponential variation starting at $x=0$ and extending to $x=T$, where the minimum index of refraction ($n=m$) is encountered.

This gives $\epsilon^{-bT}=m$ or $b=\dfrac{\log_{\epsilon}\frac{1}{m}}{T}$

Equation (12) when applied to this case gives:

$$r=\left|\frac{B_1}{A_1}\right|=\left|\frac{b}{2}\int_{x=0}^{x=T}\epsilon^{j\frac{4\pi\epsilon^{-bx}}{\lambda b}}dx\right| \tag{18}$$

or, letting $\epsilon^{-bx}=y$

$$r=\left|\frac{1}{2}\int_{y=1}^{y=m}\frac{dy}{y}\epsilon^{j\frac{4\pi y}{\lambda b}}\right| \tag{19}$$

This integral is identical in form to equation (14) and the same methods of solution hold; hence, by equation (15b) and approximations similar to those employed in Case I we have for r small and $m<<1$.

$$r=\left|\frac{B_1}{A_1}\right|=\frac{\lambda\log_{\epsilon}m}{8\pi Tm} \tag{20}$$

which holds to terms of the order of r^2.

Taking $\lambda=0.1$ *km*, $m=0.3$, $T=10$ as before, equation (20) gives $r=0.001$, a result in good accord with that previously obtained.

Case III.—$n=\dfrac{P}{X}$.

It is of interest, in conclusion, to compare the above solutions with that obtained by Rayleigh in his earlier paper. (See p. 55, ref. (21).) This solution is of particular interest because it was not obtained by use of equation (12), but by a direct investigation of the wave equation, which is solvable in this special case. (It will be noted that $s=1$ is excluded from our s power solution and has to be handled separately, due to the logarithm obtained on integrating $\dfrac{dx}{x}$.) Comparison with our results obtained above requires only a reduction of his general solution for any motion satisfying the wave equation to our special notation.

Rayleigh's problem, when reduced to the optical case and our notation, is indicated in Figure 17. Propagation is assumed in a positive direction and the variability to extend between $x=x_1$ and $x=x_2$ (we have taken $x_1=1$ and hence $x_2=\dfrac{1}{m}$ which, if T is the desired layer thickness in *km*, necessitates a unit of length of $\dfrac{T}{\frac{1}{m}-1}$ *km*).

In these units λ is related to T in km by $\lambda = (\lambda\, km)\left(\frac{\frac{1}{m}-1}{T}\right)$. In examining units in the solution as given by Rayleigh, care must be taken not to confuse our m (minimum value of n) with the m he uses, which we will designate by m' to avoid confusion.

$$\left(m' = \sqrt{\left[\frac{2\pi T}{\lambda_{km}\left(\frac{1}{m}-1\right)}\right]^2 - \frac{1}{4}}\right)$$

In our notation, Rayleigh's solution is

$$r = \left|\frac{B_1}{A_1}\right| = \sqrt{\frac{\sin^2\left(m' \log \frac{1}{m}\right)}{4m'^2 + \sin^2\left(m' \log \frac{1}{m}\right)}} \tag{21}$$

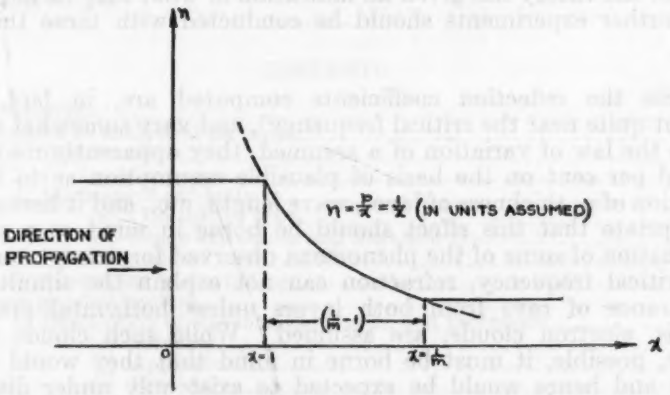

FIGURE 17.—*Form of transition assumed in investigation of reflection. (Case III)*

It is interesting to note that this solution pulsates rapidly from zero to maxima of the order of:

$$(m \angle\angle 1)\ (r \angle\angle 1)$$

$$r \doteq \frac{\lambda_{km}}{4\pi T_{km} m} \tag{22}$$

This upper bound is a result of the same order of magnitude as obtained in Cases I and II. An application of the integral given in equation (12) will indicate this property, for in this case changes of variable reduce it to a form involving an integral between limits of the form

$$K\left|\int_A^x e^{j\theta} d\theta\right|$$

which does not involve an inverse power of θ multiplying the exponential, and hence continues to pulsate reading zero at frequent intervals

over all finite but large ranges of x. Space will not be taken here for a complete discussion of this case, as tne result is obtained by Rayleigh in an independent method which offers a further check on the order of magnitude of our results obtained in the other cases. Thus equation (22) gives for $\lambda = 0.1\ km$, $T = 10\ km$, and $m = 0.3$ on upper bound of r of

$$r = 0.003$$

VI. CONCLUSIONS

The results of this paper indicate that the phenomena observed may be profitably investigated both from the point of view of refraction in the presence of two layers and from the point of view of reflection (particularly near the critical frequency f_c where the minimum value of the effective index of refraction nearly attains zero). Theoretical predictions that the most marked effects due to these causes are to be noted near the critical regions, are apparently justified by the experiments reported, which also seem to confirm the presence of two rather well-defined layers or regions of ionization. The development of the theory has given an indication of what may be looked for and further experiments should be conducted with these things in mind.

While the reflection coefficients computed are, in fact, small (except quite near the critical frequency), and vary somewhat according to the law of variation of n assumed, they apparently may reach several per cent on the basis of plausible assumption as to laws of variation of n, thickness of layer, wave length, etc., and it hence seems appropriate that this effect should be borne in mind as a possible explanation of some of the phenomena observed for, except very near the critical frequency, refraction can not explain the simultaneous appearance of rays from both layers unless horizontal gradients, that is, electron clouds, are assumed. While such clouds are, of course, possible, it must be borne in mind that they would not be stable and hence would be expected to exist only under disturbed conditions.

With present high sensitivity radio receivers, a signal ratio of 100:1 corresponding to a reflection coefficient of 0.01 should, under favorable conditions, be inconsequential provided the general signal-to-noise level were sufficiently high (that is, high power transmission under favorable conditions). Diurnal changes in sky wave energy of at least this order of magnitude are frequently observed on many frequencies.

WASHINGTON, August 21, 1931.

DETERMINATION OF INSOLUBLE MATTER IN SHELLAC

By C. C. Hartman

ABSTRACT

In existing specifications for shellac, the insoluble content is generally defined as that portion which is insoluble in hot 95 per cent ethyl alcohol, denatured with methyl alcohol. The standard methods now employed are shown to give erroneous results, caused by (*a*) incomplete solubility of the shellac wax in hot 95 per cent alcohol, (*b*) possible loss of fine particles of insoluble matter, and (*c*) retention of some of the solvent by the filter medium.

Butanol (normal butyl alcohol) and ethylene glycol-monothyl ether (cellosolve) are shown to be more satisfactory solvents for both the shellac resin and shellac wax than 95 per cent denatured alcohol. A glass-filter crucible with a disk of filter paper and an asbestos mat is a more satisfactory and efficient filtering medium than a paper extraction thimble or a series of cotton pads.

A new method is proposed in which a filter crucible and either butanol or cellosolve are used. This method is simple and rapid and yields reproducible and accurate results.

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I. INTRODUCTION

Lac resin, a secretion of the insect Tachardia lacca, is marketed under various trade names which signify the type and quality of the material. The main groups are known as stick lac, seed lac, garnet lac, button lac, flake shellac, and bleached shellac.

Stick lac represents the lac resin as it is stripped from the branches of the "host" tree. Seed lac is prepared from stick lac by crushing it into small granules, washing with dilute soda to remove a portion of the dye, and subsequently sieving to remove as much of the sticks and bark as possible. Flake shellac is a product of a crude native refining in which the melted resin is forced through cloth. The warm plastic mass is then stretched into thin sheets, which when cold are broken into fragments of different sizes. The natural coloring matter is removed by chemical treatment to produce bleached shellac.

The various kinds of shellac are sold both in the dry form and in solution in alcohol as shellac varnish. All shellac contains some insoluble matter. This insoluble matter may be present from natural sources or from intentional adulteration. Some sticks and bark are usually introduced when the shellac is stripped from the twigs and branches. Sand, dust, and other organic or inorganic materials may be incorporated by high winds, forest fires, or parasitic insects.

Misra [1] states that unscrupulous natives sometimes add shredded bark from the Babul tree, finely ground Mahua seed, rock salt, or fine sand. Arsenious sulphide is frequently added to give the shellac a lighter color.

For specification purposes, the insoluble matter should be defined as that portion insoluble in a specified solvent or solvents. Since shellac is usually sold on a specification which limits the content of insoluble matter, an accurate determination of this constituent is necessary. The present standard specifications [2] define the insoluble matter as that which is insoluble in hot 95 per cent ethyl alcohol, denatured according to either formula No. 1[3] or No. 30[4] of the Bureau of Industrial Alcohol. Owing to the incomplete solubility of shellac wax in alcohol,[5] the existing methods do not give reproducible results. This research was undertaken with the purpose of developing a more satisfactory method.

II. PRINCIPLES OF ANALYTICAL METHODS

1. REQUIREMENTS

It is essential that the method employed in this determination should be applicable to all types of lac resin. The accuracy and reproducibility may depend upon the solvent, the filtering medium, and the method and conditions of extraction. The solvent should dissolve all of the natural resin and wax. The filtering medium should permit rapid and thorough extraction of the soluble constituents and should retain all of the insoluble portion and none of the solvent. The method and conditions of extraction should be such as to insure complete extraction with a minimum of time and effort.

2. CHOICE OF SOLVENTS

The natural lac as secreted by the insect consists mainly of resin and wax. Gardner and Whitmore [6] have shown that shellac resin is completely soluble in a number of common organic liquids, but the available literature on the solubility of shellac wax is rather indefinite. From among other investigators Stillwell [7] reported the presence in shellac of about 0.5 per cent of a wax that is insoluble in hot alcohol and has a melting point of 93° C. The difficulty with the existing methods is caused chiefly by the presence of this wax. Hence an

[1] Misra, C. S., Agri. Research Inst., Pusa, Bull. No. 142, p. 54; 1923.
[2] Proc. Am. Soc. Test. Materials, 29, Pt. I, p. 656; 1929. F. S. B. Specification No. TT-S-271. U. S. Shellac Importers' Association Official Method of Analysis, p. 7; 1929.
[3] Formula No. 1 calls for the addition of 5 gallons of wood alcohol to 100 gallons of ethyl alcohol (190 proof).
[4] Formula No. 30, which calls for the addition of 10 gallons of wood alcohol to 100 gallons of ethyl alcohol (190 proof), was not used in this work.
[5] The word "alcohol" will be used hereafter to denote 95 per cent ethyl alcohol denatured according to formula No. 1.
[6] Wm. H. Gardner and W. F. Whitmore, J. Ind. Eng. Chem., vol. 21, pp. 226–229; 1929.
[7] A. G. Stillwell, J. Ind. Eng. Chem., vol. 2, p. 420; 1930.

effort was made to find a better solvent for the shellac wax both at high and low temperatures. In addition, such a solvent should be volatile at 105° C., nontoxic, and readily available in a pure state.

Butanol [8] (normal butyl alcohol) and ethylene glycol-monoethyl ether (cellosolve) were found to be the most satisfactory solvents. Quantitative data showed that both the shellac resin and the wax are completely soluble in each of these solvents.

The effect of temperature upon the solubility of the wax in different pure and mixed solvents was determined by measuring the "cloud point"; that is, the temperature at which the wax separated from the solvent. One gram samples from which all of the insoluble matter had been removed were placed in glass bottles, together with 100 ml. of the solvent to be tested. Each bottle was immersed in a water bath until the contents reached 78° C., the boiling temperature of alcohol. The source of heat was then removed and the solution was allowed to cool slowly. The solutions were observed at intervals of 0.5° C. until they became cloudy. The results are shown in Table 1. Duplicate determinations agreed within ±0.5° C.

TABLE 1.—*Cloud point of shellac in various solvents*

(1 g of shellac in 100 ml of solvent)

Experiment No.	Solvent (relative parts by volume)			Cloud point
	Alcohol	Butanol	Cellosolve	
				°C.
1	1			78
2		1		56
3			1	65
4	1	4		57
5	2	3		60
6	1		4	67
7	2		3	69

The solution in alcohol remained cloudy at the boiling point, while the butanol and cellosolve held the shellac wax in solution at a much lower temperature. As the last two liquids are good solvents for the shellac resin, they are superior to alcohol for the determination of insoluble matter. Both of these solvents can be recovered from the filtrates by direct distillation, and the distillates can be used again with accurate results.

3. METHODS OF EXTRACTION

(a) CONTINUOUS TYPE

Most of the accepted methods for determining the insoluble matter in shellac involve continuous extraction. The principal features of the methods are as follows: The method [9] of the American Society for Testing Materials specifies the boiling of 5 g of the shellac in 100 to 120 ml of alcohol for 30 minutes, filtration through a heated extraction thimble (26 by 80 mm) and extraction for one hour in a

[8] Normal butyl alcohol and ethylene glycol-monoethyl ether will be referred to, respectively, as butanol and cellosolve.

[9] Proc. Am. Soc. Test. Materials, vol. 29, pt. 1, p. 656; 1929.

siphon extractor in which the siphon is continuously surrounded by the vapors of the boiling alcohol. A metal condenser is used, and the conditions are adjusted so that the tube siphons 33 times per hour. The thimble is dried at 105° C. and weighed. The extraction is repeated until constant weight is obtained.

The United States Shellac Importers' method [10] is similar to the method of the American Society for Testing Materials, but involves the use of a glass condenser of a specified size and shape, siphoning at intervals of two minutes, and a single extraction for exactly one hour. The thimble is dried at 105° C. to constant weight.

In the Stillwell method [11] the filtering medium consists of three layers of cotton arranged on a perforated plate placed in a special type of siphon tube. The shellac is boiled in a mixture of 2 parts of alcohol and 1 part of carbon tetrachloride, filtered with suction and extracted with this mixed solvent.

(b) SINGLE EXTRACTION AND FILTRATION TYPE

If a good rapid solvent for the resin and wax is used, it should be possible to remove all of these materials in a single extraction with a considerable saving in time. Accordingly, such a method was developed for use with butanol and cellosolve. In this method a heated Jena glass-filter crucible containing a disk of filter paper and an asbestos mat is used as the filtering medium. The sample is boiled for five minutes in the solvent and filtered with suction. The crucible is washed with the boiling solvent and dried at 105° C.

III. COMPARISON OF METHODS

The above methods were used in the determination of the foreign insoluble content in three specimens of shellac. The resulting data are given in Table 2.

TABLE 2.—*Content of insoluble matter determined by various methods*

Method	Solvent	Seed lac			Flake shellac			Bleached shellac varnish		
		Insoluble			Insoluble			Insoluble		
		A	B	Average	A	B	Average	A	B	Average
		Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
A. S. T. M.	Alcohol	6.24	6.26	6.25	3.34	3.20	3.27	1.45	1.50	1.48
U. S. S. I. A.	do	6.05	6.09	6.07	3.23	3.12	3.18	1.45	1.44	1.46
Stillwell	2 parts alcohol, 1 part carbon tetrachloride.	6.86	7.08	6.97	3.08	3.06	3.07	.49	.69	.59
Heated crucible	Butanol	5.70	5.62	5.66	2.92	2.85	2.89	.25	.29	.27
	Cellosolve	5.66	5.72	5.69	2.87	2.92	2.90	.38	.27	.32

The differences in the results obtained by the various methods are doubtless due to (*a*) the temperatures of the respective solvents while in contact with the filtering medium, (*b*) differences in the

[10] Replacing method for Determination of Matter Insoluble in Hot Alcohol on pp. 7 to 12 of Official Methods of Analysis; approved by United States Shellac Importers' Association (Inc.), and American Bleached Shellac Manufacturers' Association (Inc.), issued 1929 and effective on July 1, 1930.

[11] A. G. Stillwell, J. Ind. Eng. Chem., vol. 2, p. 420; 1930.

solvent power of the respective solvents, (*c*) efficiencies of the filtering mediums.

The temperatures of the various solvents during operation were recorded. In the continuous extraction methods the temperatures of the condensed alcohol and of the alcohol-carbon tetrachloride mixture varied from 2° to 10° C. below their respective boiling points. On the other hand, the temperatures of the butanol and cellosolve solutions in the heated crucible never fell below 80° C. This temperature is well above the points at which the shellac wax starts to precipitate from these solutions. That the better results obtained with butanol or cellosolve were not entirely due to the higher temperature which was maintained in the heated crucible was shown by a number of experiments in which alcohol was used as the solvent. In these experiments the results were from 0.3 to 0.8 per cent high. The undissolved shellac wax was readily removed from the residues by means of either butanol or cellosolve.

The efficiencies of the different filter media were compared by carefully evaporating portions of the filtrates from each of these methods and making a microscopic examination of the residues. That from the Stillwell method showed an appreciable amount of fine insoluble matter and short cotton fibers. The residues from the American Society for Testing Materials and United States Shellac Importers' Association methods both showed small amounts of fine insoluble matter and paper fibers. No foreign matter of any description could be detected in the residue from the heated crucible method.

An unpublished investigation by R. T. Mease at this bureau showed that a paper extraction thimble is capable of retaining 1 per cent by weight of alcohol even after prolonged heating at 105° to 110° C. However a glass-filter crucible containing a disk of filter paper which weighed approximately 55 mg. and an asbestos mat, when treated with either butanol or cellosolve and dried for one hour at 105° to 110° C., showed no appreciable gain in weight.

In view of all the above facts, the method of the United States Shellac Importers' Association appears to be the most satisfactory of the continuous extraction methods. However, it is not possible to attain with it as good accuracy and reproducibility as with the heated crucible method.

IV. EFFECT OF SAMPLING AND GRINDING

Care must be taken to select a sample for analysis that will be representative of the shipment. Since certain types of shellac contain considerable foreign insoluble matter, every precaution should be taken that the sample is thoroughly mixed. The shellac sample should be carefully ground so as not to produce excessive heating. Even moderate heating renders some of the shellac insoluble.

The effect of the fineness of the shellac upon the reproducibility of results is shown in Table 3. Portions of dry shellac samples passing a No. 30 sieve were reground to pass a No. 40 sieve, thoroughly rolled and mixed. Duplicate determinations were made with the heated crucible method with butanol as the solvent, and the results were compared with those obtained on the samples passing a No. 30 sieve. The data show that grinding to pass a No. 40 sieve yields slightly more concordant results, probably because of the more uniform sampling thereby secured.

TABLE 3.—*Effect of fineness*

Sieve through which all the sample passed (B. S. sieve series)	Insoluble matter					
	Sample No.					
	1	2	3	4	5	6
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
No. 30	3.73	2.62	2.56	1.44	6.30	5.53
	3.78	2.68	2.65	1.39	6.45	5.62
Average	3.76	2.65	2.61	1.42	6.38	5.58
No. 40	3.80	2.68	2.55	1.40	6.43	5.44
	3.80	2.68	2.59	1.41	6.40	5.48
Average	3.80	2.68	2.57	1.41	6.42	5.46

V. RECOMMENDED METHOD

1. DESCRIPTION

(a) SOLVENTS

Either normal butyl alcohol (98 to 99 per cent) or ethylene glycol-mono-ethyl-ether (98 to 99 per cent).

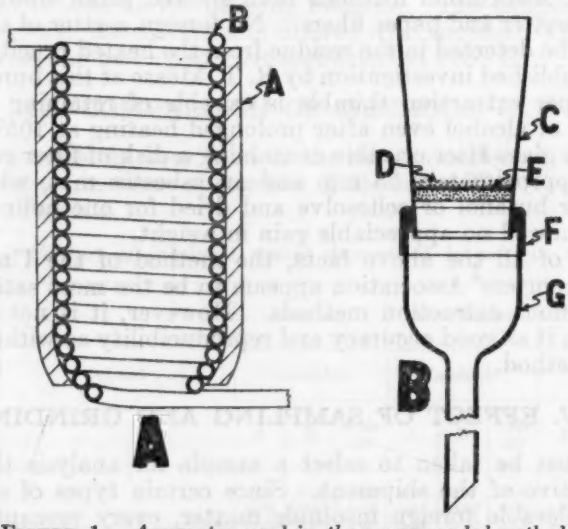

FIGURE 1.—*Apparatus used in the recommended method for the determination of insoluble matter in shellac*

A—Heating unit, *a*, sheet asbestos; *b*, copper coil.
B—Filtering unit, *c*, filter crucible; *d*, asbestos mat; *e*, disk of filter paper; *f*, rubber tubing; *g*, carbon filter funnel.

(b) APPARATUS. (See fig. 1.)

1. A Jena glass-filter crucible (*c*), (listed in Empire Laboratory Supply Co. (Inc.) catalogue as No. 8002, size No. 1), having a capacity of 30 ml, with a fritted-glass filter disk having a thickness of 3 mm and a porosity of "5 to 7" (average diameter of pores 35 μ to 40 μ).

2. A carbon filter funnel (*g*), made of pyrex glass, to fit the crucible.

3. A heating coil (*b*) made of 3 mm copper tubing of such size and shape that the filter crucible and the large part of the carbon tube will fit snugly within it.

(c) PROCEDURE

Cut a disk of filter paper (*e*) (Whatman No. 41 or equivalent) to fit inside the crucible and place it on top of the glass filter. Introduce upon the filter paper, in the customary manner, an asbestos mat (*d*) approximately 3 mm in thickness. Dry the crucible to constant weight at 105° to 110° C. and cool in a desiccator.

Weigh the prepared crucible and place it within the carbon tube, using thin rubber tubing (*f*) to form an air-tight connection. Place the combined filtering unit (*B*) within the heating unit (*A*), which is insulated on the outside with sheet asbestos (*a*), attach to a suction flask, and pass a current of steam through the coil.

Accurately weigh approximately 5 g of the dry shellac (or sufficient shellac varnish to contain about 5 g of nonvolatile matter) into a 200 ml beaker. Add 75 ml of the solvent and bring the solution to boiling on an electric stove. Keep the solution boiling slowly for five minutes to insure complete solution. Pour about 10 ml of the boiling solvent from a wash bottle into the heated crucible. Apply gentle suction and immediately pour the boiling shellac solution into the crucible in such a manner as to retain as much as possible of the insoluble residue in the beaker. Wash the insoluble residue successively with three 20 ml portions of the solvent, boiling the solution on the electric stove for about one minute before each filtration. Finally, transfer the residue from the beaker to the crucible with a stream of the boiling solvent from a wash bottle, using a "policeman" when necessary. Wash down the inner walls of the crucible with the boiling solvent. The total volume of the solvent used should be approximately 175 ml. It is advisable to keep the crucible covered with a small watch glass at all times, except when actually transferring the solution from the beaker to the crucible, or when washing down the inside walls of the crucible. By this procedure a higher temperature is maintained within the crucible.

Allow the crucible to remain within the heating coil with the suction on for a few minutes, so as to suck it as dry as possible. Remove the crucible, wash the outside with boiling solvent, and dry it in an oven at 105° to 110° C. for one hour, cool in a desiccator, and weigh. From the weight of the residue and the weight of the sample compute the percentage of insoluble matter.

The insoluble matter can be easily removed, together with the asbestos mat and filter paper. The crucible may be used several times without further cleaning. When additional cleaning is necessary, it may be easily accomplished by immersing the crucible in a hot mixture of sulphuric and nitric acids for a few minutes.

2. TYPICAL RESULTS

Several samples of dry orange shellac and bleached shellac were secured through the courtesy of J. W. Paisley and William H. Gardner, of the United States Shellac Importers' Association. In addition, two samples of bleached shellac varnish and one sample of orange shellac varnish were analyzed. These specimens were con-

sidered to be sufficiently diversified in their contents of insoluble matter to test the reliability and adaptability of the recommended method. These specimens were analyzed by the continuous-extraction method of the United States Shellac Importers' Association and the recommended method. The data are compiled in Table 4.

TABLE 4.—*Per cent of insoluble matter as determined by old and new methods*

Test sample No.	Type of material	Analyst	U. S. S. I. A. method using alcohol	Average	Recommended method using butanol	Average	Recommended method using cellosolve	Average	Average differences old minus new methods
1	Orange flake shellac (T. N.)	a	4.12		3.73		3.78		
		a	4.25		3.78		3.72		
		b	4.16		3.58				
		c	3.48	4.00	3.62	3.68		3.75	0.33
2	Orange flake shellac (Ralli U. S. S. I. A., T. N.)	a	2.90		2.68		2.63		
		a	3.00		2.63		2.70		
		b	2.60		2.61				
		c	2.65	2.79	2.64	2.64		2.66	.14
3	Orange flake shellac (N. M. I., U. S. S. I. A., T. N.)	a	2.80		2.56		2.54		
		a	2.88		2.65		2.57		
		b	2.87		2.56				
		c	2.82	2.84	2.65	2.58		2.56	.27
4	Orange flake shellac (G. R. P. Superfine)	a	1.75		1.44		1.37		
		a	1.50		1.39		1.41		
		b	1.53		1.35				
		c	1.44	1.56	1.44	1.40		1.39	.16
5	Seed lac (E. D. S. Co. Blosky)	a	6.65		6.45		6.36		
		a	6.80		6.30		6.40		
		b	6.20		6.35				
		c	5.37	6.25	6.14	6.31		6.38	−.06
6	Seed lac (L. & M. Bysacki)	a	5.80		5.53		5.54		
		a	5.65		5.62		5.44		
		b	5.34		5.38				
		c	4.75	5.38	5.19	5.43		5.49	−.05
7	Dry bleached shellac	a	.57		.06		.04		
		a	.40		.04		.09		
		b	.34		.08				
		c	.41	.43		.06		.07	.37
8	do	a	.63		.05		.09		
		a	.49		.05		.07		
		b	.50		.06				
		c	.45	.52		.05		.08	.45
9	Bleached shellac varnish	a	.97		.31		.34		.64
10	do	a	1.02		.47		.47		.55
11	Test sample No. 3 made into varnish (4 pounds to 1 gallon of alcohol)	a			2.55		2.62		

a. Author.
b. c. Analysts working in independent laboratories.

VI. CONCLUSIONS

All of the methods of the continuous extraction type require care and attention to the details of operation, even under the most favorable conditions. They consume considerable time and may give erroneous results. The chief sources of error are (*a*) incomplete solubility of the shellac wax in alcohol, (*b*) possible loss of insoluble matter from the filter medium, and (*c*) retention of some of the solvent

in the filter medium. The United States Shellac Importers Association method was found to be the most satisfactory of the methods of this type.

The resinous constituent of shellac is completely soluble in both butanol and cellosolve. The shellac wax is held in solution by either of these solvents at a much lower temperature than by alcohol.

As butanol holds the shellac wax in solution at a lower temperature than does cellosolve, it is a slightly better solvent. However, butanol is more disagreeable to work with than is cellosolve. Either of these solvents can be used with the assurance of obtaining accurate results.

The materials should be carefully samples and ground to pass a No. 40 sieve.

The heated-crucible method yields more concordant and more accurate results than the present standard methods.

The recommended method is applicable to all types of lac resins.

VII. ACKNOWLEDGMENTS

The author wishes to express his appreciation to the United States Shellac Importers Association; to J. W. Paisley, of Gillespie-Rogers-Pyatt Co. (Inc.), and W. H. Gardner, of the Shellac Research Bureau, for the courtesy extended in preparing the samples and their cooperation; and to P. H. Walker, who directed this investigation.

WASHINGTON, September 17, 1931.

RP392

DERIVATIVES OF 4-GLUCOSIDO-MANNOSE

By Horace S. Isbell

ABSTRACT

The reactions of hepta-acetyl-4-glucosido-γ-methyl-mannoside are considered in detail. It is shown that one acetyl group in hepta-acetyl-4-glucosido-γ-methyl-mannoside is resistant to alkaline hydrolysis and that it reacts with hydrogen chloride in chloroform solution to give a chloroacetyl derivative. This reaction explains the formation of the β-acetyl-methyl-glycoside which was found when the substance was treated, in dry methyl alcohol, successively with hydrogen chloride and silver carbonate. On the other hand, if moist silver carbonate is used in place of the dry salt a hexa-acetyl-4-glucosido-mannose is obtained. These reactions are indicative of the ortho ester structure.

The optical rotations of the derivatives of 4-glucosido-mannose are correlated with the rotations of the analogous derivatives of mannose. The rotations of certain derivatives of 4-glucosido-mannose corresponding to the derivatives of mannose which give exceptional rotations are likewise exceptional in respect to the numerical relations which are obtained from other sugars. Since 4-glucosido-mannose can not form a 1, 4 ring, these exceptional rotations are not caused by the existence of that structure.

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I. INTRODUCTION

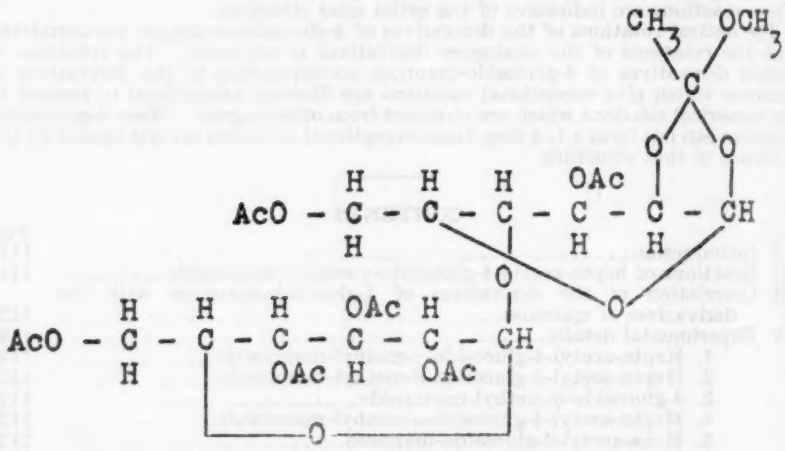
In previous publications [1] it was shown that the molecular rotations of 4-glucosido-α-mannose and 4-glucosido-β-mannose parallel the rotations of α- and β-mannose. The conclusions as to the structure of α- and β-mannose drawn from these observations were in opposition to the conclusions previously drawn by C. S. Hudson [2] from the molecular rotations of the halogen acetyl derivatives of the same sugars. These conflicting views required the extension of the comparison to include a considerable number of mannose derivatives rather than a few selected compounds.

In 1920 Fischer, Bergmann, and Rabe [3] found that three isomeric acetyl methyl rhamnosides are formed by the interaction of bromo-

[1] Isbell, B. S. Jour. Research, vol. 5 (RP253), p. 1179; 1930; also Proc. National Academy of Sciences, vol. 16, p. 704; 1930.
[2] Hudson, J. Am. Chem. Soc., vol. 52, p. 1698; 1930.
[3] Fischer, Bergmann, and Rabe, Ber., vol. 53, p. 2362; 1920.

acetyl rhamnose, methyl alcohol, and silver carbonate. Subsequently J. K. Dale [4] reported a series of closely related mannose compounds.

While recently the writer [5] reported the preparation of three isomeric hepta-acetyl-4-glucosido-methyl-mannosides from bromo-hepta-acetyl-4-glucosido-mannose by the Koenigs and Knorr reaction,[6] Haworth, Hirst, Streight, Thomas, and Webb [7] have also recently reported the preparation of hepta-acetyl-4-glucosido-α-methyl-mannoside. Consequently the writer has devoted most of his attention to the beta and gamma isomers which Haworth and his coworkers were not successful in obtaining in the crystalline state. The three new acetyl derivatives of 4-glucosido-mannose are analogous to the acetyl methyl rhamnosides and mannosides. In accordance with the nomenclature previously used for the analogous derivatives of mannose the isomer ($[\alpha[_D^{20}+=29.3$) which gives the highest dextro rota-



Hepta-acetyl-4-glucosido-γ-methyl-mannoside

tion is designated alpha; the substance ($[\alpha]_D^{20}=-23.2$) which gives the most negative rotation is designated beta; and the compound which gives the reactions characteristic of the third variety of the acetyl methyl mannosides is designated as the gamma acetyl methyl glycoside.

The gamma or third variety of the acetylated methyl rhamnoside, as well as the corresponding mannose and lyxose [8] derivatives, exhibits certain peculiar properties which led Fischer, Bergmann, and Rabe to believe that it might have a 1, 3 ring structure. However, recent methylation studies by Haworth, Hirst, and Miller [9] indicate that all three of the crystalline acetyl methyl rhamnosides have the 1, 5 ring. In order to explain the anomaly of three isomers of the same ring structure, they postulated a new type of isomerism. Shortly thereafter K. Freudenberg [10] suggested the ortho ester struc-

[4] Dale, J. Am. Chem. Soc., vol. 46, p. 1046; 1924.
[5] Isbell, J. Am. Chem. Soc., vol. 52, p. 5298; 1930.
[6] Koenigs and Knorr, Ber., vol. 34, p. 957; 1901.
[7] Haworth, Hirst, Streight, Thomas, and Webb, J. Chem. Soc., p. 2636; 1930.
[8] Levene and Wolfrom, J. Biol. Chem., vol. 79, p. 471; 1928.
[9] Haworth, Hirst, and Miller, J. Chem. Soc., p. 2469; 1929.
[10] Freudenberg, Naturwissenschaften, vol. 18, p. 393; 1930.

ture and about the same time Bott, Haworth, and Hirst [11] independently arrived at the same explanation of the new type of isomerism. The ortho ester structure of hepta-acetyl-4-glucosido-mannose is given on page 1116. This structure accounts for the interesting properties of the substance which are considered in the next paragraph.

II. REACTIONS OF HEPTA-ACETYL-4-GLUCOSIDO-γ-METHYL-MANNOSIDE

The ortho esters, such as trimethyl ortho acetic ester, are fairly resistant to alkaline hydrolysis, but they are very easily hydrolyzed by acids. Previously Fischer, Bergmann, and Rabe, as well as Dale, had found that one acetyl group in their gamma acetyl methyl glycosides was resistant to alkaline hydrolysis. Hepta-acetyl-4-glucosido-γ-methyl-mannoside also exhibits this peculiar property which is characteristic of the ortho esters. Thus, six acetyl groups in the new substance are easily removed by either acids or alkalies, but the seventh is resistant to alkaline hydrolysis.

The reactions of these ortho sugar derivatives with hydrogen chloride are of unusual interest. Previously Dale had observed that a rapid change in specific rotation is produced by the addition of hydrogen chloride to a methyl alcoholic solution of tetra-acetyl-γ-methyl-mannoside. Under similar conditions the writer found an analogous change in the specific rotation of hepta-acetyl-4-glucosido-γ-methyl-mannoside. Curves *III* and *II* in Figure 1 illustrate the changes caused in the specific rotations of tetra-acetyl-γ-methyl-mannoside and hepta-acetyl-4-glucosido-γ-methyl-mannoside by the addition of two equivalents of hydrogen chloride in dry methyl alcoholic solution. In each case the rotation changes very quickly from a negative to a positive value. Previously it was believed that the change in rotation was caused by a shift in ring structure involving a migration of an acetyl group.[12] The evidence for this interpretation was the experimental fact, discovered by Dale,[13] that tetra-acetyl-β-methyl-mannoside may be obtained from tetra-acethyl-γ-methyl-mannoside after treatment with an alcoholic solution of hydrogen chloride. The hydrogen chloride was removed with silver carbonate and the resulting solution gave about a 7 per cent yield of crystalline tetra-acetyl-β-methyl-mannoside. By the same procedure the writer was able to obtain hepta-acetyl-4-glucosido-β-methyl-mannoside from the gamma acetyl methyl glycoside. The isolation of these products does not explain the change in rotation observed after the addition of hydrogen chloride because the specific rotations of the beta-acetyl methyl glycosides are more negative than the rotations of the corresponding gamma derivatives. Obviously, in order to change the rotation from a negative value to a positive value, a substance, or substances, of positive rotation must be formed. The reaction may involve many factors, including the solvent and silver carbonate; hence the experimental conditions were altered so as to eliminate the use of silver carbonate and methyl alcohol. When a chloroform solution of hepta-acetyl-4-glucosido-γ-methyl-mannoside is treated with hydrogen chloride, a rapid change in rotation occurs, as may

[11] Bott, Haworth, Hirst, J. Chem. Soc., p. 1395; 1930.
[12] Hudson, J. Am. Chem. Soc., vol. 48, p. 1433; 1926.
[13] See footnote 4, p. 1116.

be seen in Curve *I* of Figure 1. This change in rotation is similar to that observed with alcoholic solutions. The chloroform solution gives on evaporation chloro-hepta-acetyl-4-glucosido-mannose. This substance gives a positive rotation which explains the changes in rotation previously noted. Inasmuch as the methyl glycosides are conveniently prepared by the use of a small quantity of hydrogen chloride in methyl alcoholic solution, one would not expect a true methyl glycoside to yield the chloro-acetyl derivative under the conditions given above.

Before turning to the interpretation of this reaction in relation to the ortho ester structure, we will consider the reaction of hepta-acetyl-4-glucosido-γ-methyl-mannoside with moist hydrogen chloride. When hepta-acetyl-4-glucosido-γ-methyl-mannoside is treated, first with dry hydrogen chloride in methyl alcohol, and then with moist

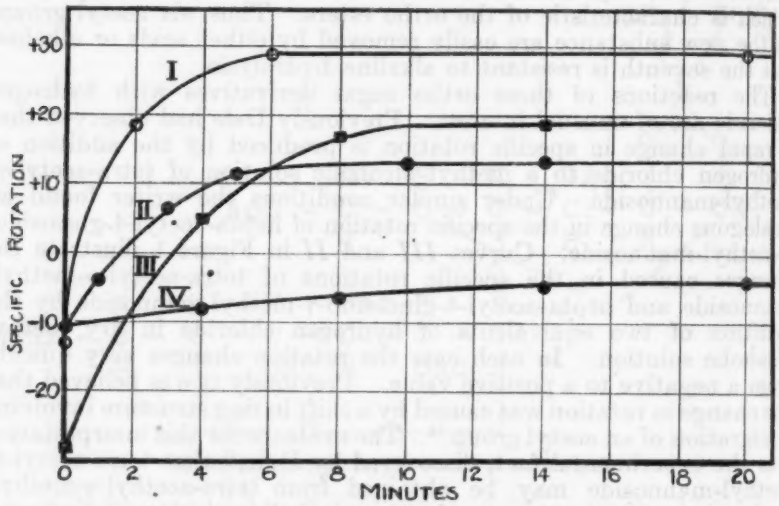


FIGURE 1.—*Changes in specific rotation after the addition of two equivalents of hydrogen chloride to 0.05 N solutions of the acetylated γ-methyl glycosides*

I, Hepta-acetyl-4-glucosido-γ-methyl-mannoside in chloroform.
II, Hepta-acetyl-4-glucosido-γ-methyl-mannoside in methyl alcohol.
III, Tetra-acetyl-γ-methyl-mannoside in methyl alcohol.
IV, Hepta-acetyl-4-glucosido-γ-methyl-mannoside in 80 per cent aqueous methyl alcohol.

silver carbonate, hexa-acetyl-4-glucosido-mannose[14] is obtained in good yield.

The structure of the new hexa-acetyl-4-glucosido-mannose has not been rigidly determined.[15] Since the normal acetylated methyl glycosides are not appreciably altered, under the conditions used in the preparation of the hexa-acetate, probably the six normal acetyl groups in the parent hepta-acetyl-4-glucosido-γ-methyl-mannoside would remain intact. Inasmuch as the ortho acetates are very easily decomposed by acids the simplest explanation for the formation of the hexa-acetyl-4-glucosido-mannose is that the ortho acetate group is

[14] This product was obtained in an attempt to prepare ortho-hepta-acetyl-4-glucosido-mannose, and it was reported as such in a preliminary note in the J. Am. Chem. Soc., vol. 52, p. 5298; 1930.

[15] What appears to be an analogous derivative of mannose has been obtained by the method used in the preparation of hexa-acetyl-4-glucosido-mannose. It is anticipated that this substance may be used for the synthesis of disaccharides and other sugar derivatives. These phases of the subject as well as the structure of the substance are being investigated.

split off. This would give a 1, 2 unsubstituted hexa-acetyl-4-glucosido-mannose. This substance contains a free carbonyl group, and, hence, one would expect it to exhibit mutarotation. The new hexa-acetate does not exhibit mutarotation in methyl alcohol or glacial acetic acid, but it does exhibit a very slight mutarotation in pyridine. The absence of mutarotation, in the solvents first mentioned, is exceptional if the substance is a single form of the sugar containing a free reducing group. On acetylation with acetic anhydride and pyridine at low temperatures it gives a good yield of α-octa-acetyl-4-glucosido-mannose. Since these reagents do not usually cause any marked changes in structure, the formation of this normal octa-acetate indicates that the original substance is a normal hexa-acetate instead of an ortho acetate. This conclusion is also supported by the fact that the hexa-acetate, as well as the octa-acetate, gives on hydrolysis with acid the same acetyl value as is obtained with alkali. Normal acetates give like values on hydrolysis with acids and alkalies, but usually ortho acetates give different values.

Hexa-acetyl-4-glucosido-mannose may be obtained also without the use of moist silver carbonate by the addition of water to the solution of hepta-acetyl-4-glucosido-γ-methyl-mannoside which has been previously treated with dry hydrogen chloride dissolved in methyl alcohol. But when hepta-acetyl-4-glucosido-γ-methyl-mannoside was treated with an aqueous methyl alcoholic solution of hydrogen chloride no crystalline hexa-acetate was obtained. The reaction was incomplete because a portion of the hepta-acetyl-4-glucosido-γ-methyl-mannoside was reclaimed unchanged. The change in the optical rotation of the aqueous alcoholic solution is illustrated in Curve *IV*, Figure 1, page 1118. It is evident from the curve that the change is less rapid than that found for the chloroform and anhydrous methyl alcoholic solutions.

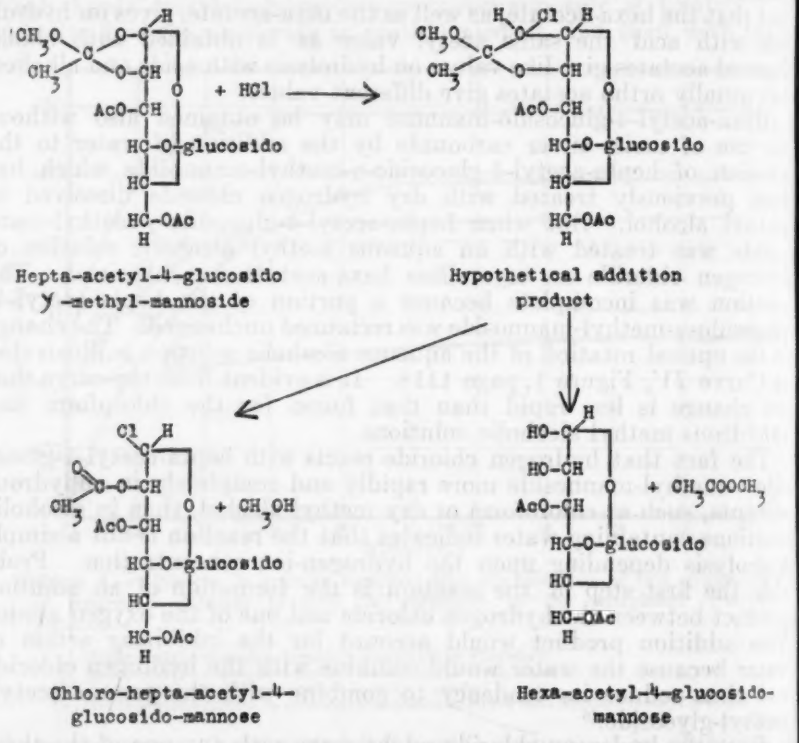
The fact that hydrogen chloride reacts with hepta-acetyl-4-glucosido-γ-methyl-mannoside more rapidly and completely in anhydrous solvents, such as chloroform or dry methyl alcohol, than in alcoholic solutions containing water indicates that the reaction is not a simple hydrolysis depending upon the hydrogen-ion concentration. Probably the first step in the reaction is the formation of an addition product between the hydrogen chloride and one of the oxygen atoms. This addition product would account for the inhibiting action of water because the water would combine with the hydrogen chloride and thus reduce its tendency to combine with the gamma-acetyl-methyl-glycoside.[16]

Since the hydrogen chloride might react with any one of the three oxygen atoms in the ortho ester group the reaction could proceed in several ways. If the hydrogen chloride united with the oxygen atom combined with the first carbon atom of the sugar, the addition product would give chloro-hepta-acetyl-4-glucosido-mannose by the elimination of methyl alcohol. This explains the formation of the chloro-acetyl derivative in chloroform solution. On the other hand, if the reaction be reversible, the addition of a considerable quantity of methyl alcohol would decrease the tendency to eliminate methyl alcohol, hence, under these conditions the chloro-acetyl derivative

[16] The inhibiting effect of the water in this case is somewhat analogous to the inhibiting effect of water on the addition reactions of anhydrous auric chloride. (Kharasch and Isbell, J. Am. Chem. Soc., vol. 53, p. 3055; 1931.)

would not be formed in as large amounts. When methyl alcohol was used as a solvent it was not possible to obtain any crystalline chloro-hepta-acetyl-4-glucosido-mannose, but even so, a small quantity of the chloro-acetyl derivative might have been formed which would react with the dry silver carbonate to give the hepta-acetyl-4-glucosido-β-methyl-mannoside which was separated in small amounts. Furthermore, by reaction with water the hydrogen chloride addition product might be decomposed with the elimination of hydrogen chloride and methyl acetate to give hexa-acetyl-4-glucosido-mannose. The reactions are illustrated below.

Another reaction of hepta-acetyl-4-glucosido-γ-methyl-mannoside, somewhat analogous to that with hydrogen chloride, was observed in



an attempt to prepare the acetylated alpha methyl glycoside. A chloroform solution of hepta-acetyl-4-glucosido-γ-methyl-mannoside was treated with titanium tetrachloride in the manner which Pacsu[17] has found gives a satisfactory transformation of hepta-acetyl-β-methyl-cellobioside into the corresponding alpha isomer. The product was not the isomeric alpha derivative, but chloro-hepta-acetyl-4-glucosido-mannose.[18] Thus it is seen that the gamma-acetyl-methyl glycosides on treatment with titanium tetrachloride do not give the reactions characteristic of the true acetyl methyl glycosides.

[17] Pacsu, J. Am. Chem. Soc., vol. 52, p. 2571; 1930.
[18] This reaction is somewhat similar to the reaction of titanium tetrachloride with the fully acetylated sugar which has been studied by Pacsu (Ber., vol. 61, p. 1508; 1928).

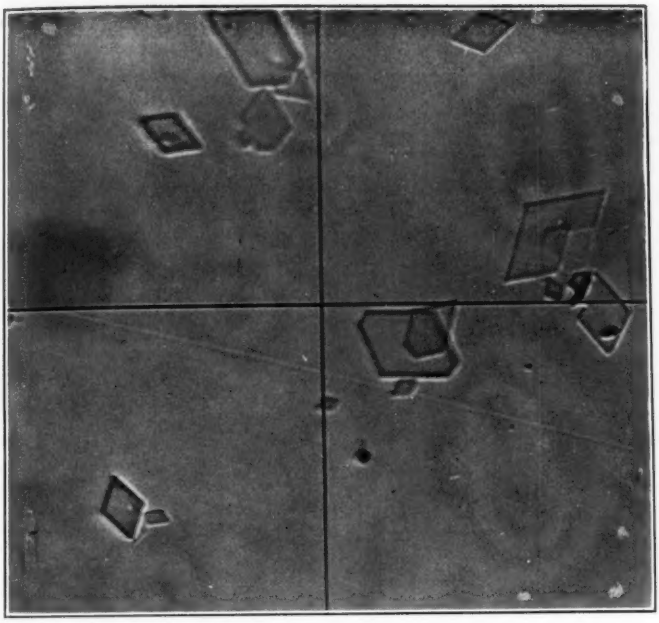


FIGURE 2.—*Hepta-acetyl-4-glucosido-γ-methyl-mannoside*

FIGURE 3.—*Hepta-acetyl-4-glucosido-γ-methyl-mannoside*
Crystallized from methyl alcohol.

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Another peculiar property of hepta-acetyl-4-glucosido-γ-methyl-mannoside is that it gives two decidedly different crystalline forms. It was first obtained in thin tabular crystals, illustrated in Figure 2. When these crystals are dissolved in the proper quantity of methyl alcohol and allowed to stand a few minutes, a second crystalline form separates from the solution. The second form crystallizes in slender rectangular prisms, as shown in Figure 3. The latter substance may be reconverted into the first by recrystallization from hot amyl alcohol. After mild drying both substances give essentially the same melting points and specific rotations. The existence of this change in form, whatever it may be, suggests that the sugar derivatives exist in solution in various forms, perhaps, loosely combined with the solvent and that the structure of the substance which crystallizes from solution may be determined at least occasionally by the solvent employed.[19]

III. CORRELATION OF THE DERIVATIVES OF 4-GLUCOSIDO-MANNOSE WITH THE DERIVATIVES OF MANNOSE

The optical rotations of many of the derivatives of mannose do not follow the same numerical relationships which are found in the glucose series.[20] The exceptional rotations show that either there are unusual differences in structure or else the theory of optical superposition is not valid. In a previous publication [21] it was shown that the optical rotations of 4-glucosido-α-mannose and 4-glucosido-β-mannose parallel the rotations of α-and-β-mannose, which indicates that 4-glucosido-α-mannose has the α-mannose structure while 4-glucosido-β-mannose has the β-mannose structure. In this paper additional derivatives of 4-glucosido-mannose are reported and correlated with the derivatives of mannose. The existence of these derivatives of 4-glucosido-mannose, a sugar which can not form a 1, 4 ring, clearly shows that the exceptional rotations are not caused by the 1, 4 ring structure.

TABLE 1.—*Acetyl methyl glycosides of mannose, rhamnose, and 4-glucosido-mannose*

	Type	Melting point	Molecular weight	$[\alpha]_D$[a]	[M]
		°			
Tetra-acetyl-α-methyl-*d*-mannoside [b]	1, A	65	362	+49.1	+17,770
Hepta-acetyl-4-glucosido-α-methyl-*d*-mannoside	1, A	185	650	+29.3	+19,050
Tri-acetyl-α-methyl-*l*-rhamnoside [c]	1, A	87	304	−53.5	[d] −16,260
Tetra-acetyl-β-methyl-*d*-mannoside [b]	1, B	161	362	−46.8	−16,940
Hepta-acetyl-4-glucosido-β-methyl-*d*-mannoside	1, B	178	650	−23.2	−15,080
Tri-acetyl-β-methyl-*l*-rhamnoside [c]	1, B	152	304	+45.7	[d] +13,890
Tetra-acetyl-γ-methyl-*d*-mannoside [b]	1, C	105	362	−26.6	−9,630
Hepta-acetyl-4-glucosido-γ-methyl-*d*-mannoside	1, C	167	650	−12.7	−8,260
Tri-acetyl-γ-methyl-*l*-rhamnoside [c]	1, C	85	304	+28.0	[d] +8,510

[a] The values given are for chloroform solutions except for the derivatives of rhamnose which are given for acetylene tetra-chloride solutions.

[b] Dale, J. Am. Chem. Soc., vol. 46, p. 1046; 1924.

[c] Fischer, Bergmann, and Rabe, Ber., vol. 53, p. 2362; 1920.

[d] Reversing the signs of the rotations of the *l*-rhamnose derivatives gives the rotations in the *d*-rhamnose series. Such rotations are comparable with the rotations of the *d*-mannose, and 4-glucosido-*d*-mannose derivatives, because *d*-rhamnose and *d*-mannose have similar structures.

[19] In a previous publication (B. S. Jour. Research, vol. 5 (RP226), p. 748) the writer has shown that the equilibrium between the various forms of *d*-gulose $CaCl_2$ may be altered by changing the solvent.

[20] Hudson, J. Am. Chem. Soc., vol. 48, p. 1434; 1926.

[21] See footnote 1, p. 1115.

TABLE 2.—*Acetyl derivatives of mannose and 4-glucosido-mannose*

	Molecular weight	$[\alpha]_D$	[M]
Fluoro-tetra-acetyl-*d*-mannose [1]	350	+21.5	+7,530
Fluoro-hepta-acetyl-4-glucosido-mannose [2]	638	+13.6	+8,680
Chloro-tetra-acetyl-*d*-mannose [3]	367	+89.5	+32,850
Chloro-hepta-acetyl-4-glucosido-*d*-mannose [3]	655	+51.2	+33,540
Bromo-tetra-acetyl-*d*-mannose [1]	411	+131.6	+54,090
Bromo-hepta-acetyl-4-glucosido-*d*-mannose [2]	699	+77.9	+54,450
Iodo-tetra-acetyl-*d*-mannose [1]	458	+190.5	+87,250
Iodo-hepta-acetyl-4-glucosido-*d*-mannose [3]	746	+111.5	+83,180
α-Penta-acetyl-*d*-mannose [4]	390	+55	+21,450
α-Octa-acetyl-4-glucosido-*d*-mannose [3]	678	+36.2	+24,540
β-Penta-acetyl-*d*-mannose [4]	390	−25.3	−9,870
β-Octa-acetyl-4-glucosido-*d*-mannose [3]	678	−13.0	−8,810

[1] Brauns, B. S. Jour. Research, vol. 7 (RP358), p. 573; 1931.
[2] Brauns, J. Am. Chem. Soc., vol. 48, p. 2776; 1926.
[3] Brauns, J. Am. Chem. Soc., vol. 44, p. 401; 1922.
[4] Hudson and Dale, J. Am. Chem. Soc., vol. 37, p. 1280; 1915.

TABLE 3.—*Molecular rotations of mannose derivatives*

	Molecular weight	$[\alpha]_D$	[M]
α-*d*-Mannose [1]	180	+30	+5,400
4-Glucosido-α-mannose [2] (monohydrate)	360	+14.6	+5,260
β-*d*-Mannose [1]	180	−17	−3,060
4-Glucosido-β-mannose	342	−6.5	−2,220
α-Methyl-*d*-mannoside [4]	194	+79	+15,330
4-Glucosido-α-methyl mannoside [5]	356	+46	+16,380

[1] Levene, J. Biol. Chem., vol. 57, p. 329; 1923; vol. 59, p. 129; 1924.
[2] Isbell, B. S. Jour. Research, vol. 5 (RP253), p. 1186; 1930.
[3] Hudson and Yanovski, J. Am. Chem. Soc., vol. 39, p. 1013; 1917.
[4] Van Ekenstein, Rec. trav. chim., vol. 15, p. 223; 1896.
[5] Haworth, Hirst, Streight, Thomas, and Webb, J. Chem. Soc., p. 2639; 1930.

A comparison of the molecular rotations of the acetyl methyl glycosides of mannose, rhamnose, and 4-glucosido-mannose is given in Table 1. Each of the three sugars forms three acetyl methyl glycosides exhibiting analogous chemical and physical properties. It is apparent, without any involved calculations, that the derivatives of the various sugars bear the same relationship to one another in the three series. The molecular rotations of the α-, β-, and γ-acetylated methyl glycosides of 4-glucosido-mannose differ from the molecular rotations of the α, β, and γ mannose derivatives by +1,280, +1,860, and +1,370, respectively. These values show that the acetylated 4-glucosido-mannose chain [22] is slightly more dextrorotatory than the mannose chain.

As illustrated in Table 2 this correlation in molecular rotations is not restricted to the acetylated methyl glycosides, but is also found in the halogen acetyl derivatives and in the acetylated sugars. The molecular rotations of the halogen acetyl derivatives of 4-glucosido-

[22] The rotation of the 4-glucosido-mannose chain is composed of the rotation of the primary mannose group and the secondary glucose residue. The approximate agreement of its molecular rotation with the rotation of the mannose chain is the result of compensation; that is, the dextro rotating glucose residue is compensated for by its β-glucosidic union.

mannose differ from the molecular rotations of the corresponding derivatives of mannose by +1,150, +690, +360, and −4,070, respectively, for the fluorides, chlorides, bromides, and iodides. These values are of the same order as those obtained from the acetylated glycosides and indicate that the rotation of the acetylated 4-glucosido-mannose chain is only slightly different from the rotation of the acetylated mannose chain. However, the differences between the rotations of corresponding derivatives of 4-glucosido-mannose and mannose decrease progressively from fluorine to iodine. This is additional evidence in support of the writer's previous statement [23] that a change in the first carbon produces small but definite changes in the rotation of the rest of the molecule. The molecular rotation of penta-acetyl-mannose (+21,450) has been considered exceptional,[24] hence the comparison of its rotation with the rotation of the closely related substance, octa-acetyl-4-glucosido-mannose (+24,540), is of particular interest. The difference in the molecular rotations of the substances just mentioned (+3,090), as well as the difference between the molecular rotations of the β-forms (+1,060), is in fair agreement with the values derived from the acetylated methyl glycosides and from the halogen acetyl derivatives.

The rotations of some unacetylated derivatives of mannose and 4-glucosido-mannose are given in Table 3. The differences between the molecular rotations of the corresponding derivatives of 4-glucosido-mannose and mannose are −140, +840, and +1,050, respectively, for the α- and β-forms of the sugars and the α-methyl glycosides. The average of these differences shows that the unacetylated derivatives of 4-glucosido-mannose are usually slightly more dextrorotatory than the corresponding derivatives of mannose. It will be recalled that a similar relation was found for the acetyl derivatives.

The difference between the molecular rotations of the α- and β-forms of 4-glucosido-mannose is +7,480. This value is of the same order as the value +8,460 obtained for the difference in the molecular rotations of α- and β-mannose. The latter value has long been recognized as different from the value +17,000 [25] obtained from many other sugar derivatives. Anomalous values are also found for the acetylated methyl glycosides. The differences between the molecular rotations (Table 1) of the α- and β-acetyl methyl glycosides of mannose, rhamnose, and 4-glucosido-mannose are +34,710, +30,150, and +34,130, respectively, which are widely different from the values +53,900, +53,460, and +52,300, obtained from the α- and β-acetyl methyl glucosides, galactosides, and xylosides.[26] Similar variations are found in the differences between the molecular rotations of the acetylated sugars. Thus the difference between the molecular rotations of the two forms of octa-acetyl-4-glucosido-mannose is +33,350, which is of the same order as the value (+31,200) obtained by Hudson [27] from the corresponding derivatives of mannose. These values are also close to the value (+32,700) derived by him from one pair of his *d*-galactose penta-acetates,[28] but they differ widely from the values obtained from many other sugars.

[23] Isbell, B. S. Jour. Research, vol. 5 (RP253), p. 1184; 1930.
[24] Hudson, J. Am. Chem. Soc., vol. 48, p. 1433; 1926.
[25] Hudson, J. Am. Chem. Soc., vol. 48, p. 1424; 1926.
[26] Dale and Hudson, J. Am. Chem. Soc., vol. 52, p. 2534; 1930.
[27] Hudson, B. S. Sci. Paper No. 533, p. 259; 1926.
[28] It is possible that the four penta-acetates of galactose do not represent two pairs of ring isomers, as previously believed, but that they differ in some manner as yet not clearly understood.

The difference between the molecular rotations of 4-glucosido-α-methyl-mannoside (+16,380) and 4-glucosido-β-methyl-mannoside (−17,700) is approximately +34,000. This value is only slightly less than the value (+37,500) obtained in the glucose series. Since β-methyl-mannoside is not known in the crystalline state the analogous value in the mannose series is not available. Inasmuch as the 4-glucosido-β-methyl-mannoside is somewhat peculiar, in that it seemingly contains 1 molecule of water for each 2 molecules of the glycoside, further experimental work is necessary before any conclusions may be drawn from its rotation.

In the preceding pages it has been shown that the rotations of certain derivatives of 4-glucosido-mannose, corresponding to the derivatives of mannose which give abnormal rotations, are likewise unusual in respect to the numerical relations which are obtained from many other sugars. The existence of the derivatives of 4-glucosido-mannose which give abnormal rotations clearly shows that these "exceptional" values are not caused by a 1, 4 oxygen ring.

IV. EXPERIMENTAL DETAILS

1. HEPTA-ACETYL-4-GLUCOSIDO-γ-METHYL-MANNOSIDE

Twenty-five grams of bromo-hepta-acetyl-4-glucosido-mannose was mixed at 0° C. with 25 g of dry freshly prepared silver carbonate in 250 ml of anhydrous methyl alcohol. After being shaken for 30 minutes the solution was filtered. The filtrate, which gave a negative halogen test, was concentrated in vacuo to a thick sirup. After the addition of a small quantity of ether a crystalline product was separated. As shown in Figure 2, the substance crystallizes under these conditions in plates which frequently appear as diamonds or hexagons. This substance is hepta-acetyl-4-glucosido-γ-methyl-mannoside. The mother liquor was evaporated to a sirup from which several small fractions of crystalline material were obtained by alternate addition of ethyl alcohol and evaporation. Seventeen grams of crystalline material was obtained, which contained the β and γ isomers. By fractional crystallization from ethyl alcohol 14 g of the γ compound was separated. After drying at 50° in vacuo it melted at 167° C. and gave a specific rotation of −12.9. After two additional crystallizations it melted at the same temperature and in chloroform solution gave $[\alpha]_D^{20} = -12.7$ (0.6432 g substance dissolved in 20 ml of chloroform read −2.36° S., 2-dm tube). Analysis calculated for $C_{27}H_{38}O_{18}$: C, 49.82; H, 5.89. Found: C, 50.07; H, 5.96.

The compound (0.4046 g) was refluxed 4 hours with 50 ml of 0.25 *N*, sulphuric acid. The back titration with standard alkali gave a value which was equivalent to an increase of 43.3 ml of 0.1 *N* acid. This equals 64.25 per cent acetic acid, while that calculated for completely hydrolyzed hepta-acetyl-4-glucosido-methyl-mannoside is 64.62 per cent. Hydrolysis with alkalies gave a different result. The percentage of acetic acid obtained by alkaline hydrolysis corresponds to the quantity calculated by assuming the hydrolysis of only six acetyl groups. A 0.1417 g sample was shaken with 50 ml of 0.1 *N* barium hydroxide solution for 2 hours and allowed to stand for 18 hours in the refrigerator. The back titration with standard hydrochloric acid showed that 13.1 ml of 0.1 *N* acid was formed by

hydrolysis. This equals 55.50 per cent acetic acid while that calculated for the hydrolysis of six acetyl groups is 55.39 per cent.

Hepta-acetyl-4-glucosido-γ-methyl-mannoside (0.4137 g) was dissolved in sufficient methyl alcohol to give a volume of 11 ml; the specific rotation was then −10.5. After the addition of 0.5 ml of methyl alcohol, containing 0.043 g of hydrogen chloride, the following specific rotations were observed after 1, 3, 5, and 10 minutes, respectively: −4.1, +7.2, +11.2, and +12.8. After 10 minutes the rotation was virtually constant as no further change was observed during the day.

The tabular crystals of hepta-acetyl-4-glucosido-γ-methyl-mannoside on recrystallization from methyl alcohol give a second crystalline product which separates in slender rectangular prisms. About 0.35 g of finely powdered hepta-acetyl-4-glucosido-γ-methyl-mannoside was dissolved in 5 ml of methyl alcohol. Solution was complete in about one minute and in a few minutes a new crystalline form of hepta-acetyl-4-glucosido-γ-methyl-mannoside separated from the solution. (Fig. 3.) It was collected upon a filter and washed with a small quantity of methyl alcohol. On evaporation of the mother liquor additional material was obtained, the final yield being nearly quantitative. The substance after drying one hour at 40° in vacuo melted at 165° to 167° (not sharp), and in chloroform $[\alpha]_D^{20} = -13.2$ (0.3408 g substance dissolved in 10 ml read −2.60° S. in a 2 dm tube). Analysis calculated for $C_{27}H_{38}O_{18}$: C, 49.82, H; 5.89. Found: C, 49.73; H, 5.98.

A quantity of the prismatic crystals was dissolved in a small amount of hot amyl alcohol; on cooling the substance separated in tabular crystals which seemed identical with the form first described. The tabular form was also obtained by recrystallizing the prismatic form from chloroform and from ether.

2. HEPTA-ACETYL-4-GLUCOSIDO-β-METHYL-MANNOSIDE

The material which remained after the crystallization of the γ compound consisted of the β derivative mixed with some γ compound. The β compound is slightly less soluble in water and in ethyl alcohol than the γ compound, but even so the separation of the two substances is difficult. The nearly pure β compound was obtained by crystallizing the impure product, first from water and then from absolute ethyl alcohol. It crystallizes in prisms which are frequently very slender, but under favorable conditions they become wider and thicker. The melting point is 178° and the taste very bitter.

The product, after drying at 50° in vacuo, gave in chloroform solution $[\alpha]_D^{20} = -22.3$ (0.6563 g of the compound dissolved in 25 ml read −3.38° S. in a 2 dm tube). Analysis calculated for $C_{27}H_{38}O_{18}$: C, 49.82; H, 5.89. Found: C, 49.54; H, 5.75.

As described in the next paragraph hepta-acetyl-4-glucosido-β-methyl-mannoside was deacetylated and crystalline 4-glucosido-β-methyl mannoside was prepared. This substance on acetylation regenerates pure hepta-acetyl-4-glucosido-β-methyl-mannoside, which after recrystallization melts at 178° and gives $[\alpha]_D^{20} = -23.2$.

3. 4-GLUCOSIDO-β-METHYL-MANNOSIDE

This substance was obtained from its hepta-acetate by deacetylation with barium methylate.[29] The acetylated glycoside (1.5 g) was dissolved in 30 ml of cold methyl alcohol; after the addition of 2 ml of 0.4 *N* barium methylate it was allowed to stand 24 hours in the refrigerator. The barium was then precipitated with sulphuric acid and removed by filtration. The filtrate was evaporated in vacuo to a thick sirup from which the new substance separated in slender prismatic crystals. The crystalline material (0.7 g) was triturated with absolute ethyl alcohol and collected upon a filter. It was then recrystallized from 95 per cent alcohol. It is very soluble in water and moderately soluble in hot ethyl alcohol. After two crystallizations it melted at 229° C. This melting point was not changed by further crystallization. It gave in water solution $[\alpha]_D^{20} = -48.5$ (0.4063 g dissolved in 10 ml read −11.38° S. in a 2 dm tube.) The specific rotation in water for the mercury green line ($\lambda = 5{,}461$) was found to be −55.7.

The substance was dried at 60° in vacuo. Analysis calculated for $(C_{13}H_{24}.O_{11})_2.H_2O$: C, 42.72; H, 6.90. Found: C, 42.90; 42.94; H, 6.83, 6.83. The analysis of the compound indicates that it is slightly impure or else that it contains 1 molecule of water for each 2 molecules of the glycoside. It does not lose water at 100° in vacuo which indicates that the water, if present, is held tightly.

The new compound gives hepta-acetyl-4-glucosido-β-methyl-mannoside in good yield on acetylation. About 0.3 g of the substance was mixed with a cold solution of 2 ml of acetic anhydride and 2.5 ml of pyridine and allowed to stand 20 hours in the refrigerator. The mixture was then poured into ice water, and the product separated by extraction with chloroform; after the customary washing, drying, and evaporation about 0.5 g of crystalline hepta-acetyl-4-glucosido-β-methyl-mannoside was obtained. After recrystallization from ethyl alcohol it melted at 178° and gave $[\alpha]_D^{20} = -23.2$ (0.4702 g dissolved in 10 ml of chloroform read −6.31° S. in a 2 dm tube). This specific rotation is slightly more negative than that obtained for the sample of hepta-acetyl-4-glucosido-β-methyl-mannoside described in the previous paragraph. Inasmuch as the melting point of either sample is not lowered by the addition of the other the two products are the same; consequently the original hepta-acetyl-4-glucosido-β-methyl-mannoside was not fundamentally altered by deacetylation.

The deacetylated product is probably a hydrated 4-glucosido-β-methyl-mannoside. It will be investigated further, the small amount of material on hand preventing additional study at this time.

4. HEPTA-ACETYL-4-GLUCOSIDO-α-METHYL-MANNOSIDE

This product was obtained from the mother liquor which remained after the separation of the β and γ isomers. After all of the solvent was removed the residue was triturated with about 25 ml of absolute methyl alcohol and the mixture, which contained some crystalline material, was allowed to stand. After several days 0.5 g of crystalline material had separated. Under the microscope the crystals appear as thin diamond-shaped prisms. Analysis calculated for $C_{27}H_{38}O_{18}$: C, 49.82; H, 5.89. Found: C, 49.81; H, 5.96. After the product was

[29] Isbell, B. S. Jour. Research, vol. 5 (RP253), p. 1185; 1930.

recrystallized from methyl alcohol it melted at 185° and gave $[\alpha]_D^{20} = +26.7$. Two other preparations of the same substance melted at 184° to 185° and gave slightly higher specific rotations (+28.9, +28.5). They were combined and recrystallized from methyl alcohol. the resulting product melted at 185° and gave $[\alpha]_D^{20} = +29.3$ in chloroform. (0.2105 g of the compound dissolved in 10 ml of chloroform read +3.56° S. in a 2 dm tube.) The small amount of material on hand prevented further study of the substance which has also been prepared very recently by Haworth, Hirst, Streight, Thomas, and Webb. They report the melting point as 184° and $[\alpha]_D^{20} = +30$.

A considerable amount of material remained after the separation of the α, β, and γ isomers. The methyl alcohol was removed and the residue (about 5 g) was dissolved in amyl alcohol. The solution, after cooling to 0°, gave a low melting crystalline product. The crude product melted near room temperature and in chloroform solution gave $[\alpha]_D^{20} = +15$. This residual product may contain one or more additional substances which have not been separated.

5. HEXA-ACETYL-4-GLUCOSIDO-MANNOSE

A 5 g sample of hepta-acetyl-4-glucosido-γ-methyl-mannoside was suspended in 50 ml of cold absolute methyl alcohol and 4 ml of methyl alcohol containing 0.34 g of dry hydrogen chloride were added. The flask was shaken until solution was complete (about one minute) and then allowed to stand at room temperature. After 10 minutes the acid solution was mixed with a paste consisting of 10 g of silver carbonate and 2 ml of water. The mixture was stirred until a negative test for halogens was obtained, when the silver salts were removed by filtration. The solution was next evaporated in vacuo to a thick sirup which crystallized in the course of several days. The new substance crystallizes in rectangular prisms. It is difficultly soluble in water, fairly soluble in ether, and very soluble in chloroform. The crude material (3.8 g) was recrystallized from hot ethyl alcohol. The resulting product melted at 171°. The melting point is not very sharp, but it could not be changed by recrystallization from alcohol or from ethyl acetate by the addition of petroleum ether.

The optical rotation was determined in chloroform, methyl alcohol, glacial acetic acid and pyridine solutions. The recrystallized compound gave in chloroform solution $[\alpha]_D^{20} = +21.7$ (0.6040 g of the substance dissolved in 25 ml read +3.03° S. in a 2 dm tube); methyl alcohol, $[\alpha]_D^{20} = +14.6$ (0.5325 g of the substance dissolved in 25 ml 4 minutes after solution, read 1.80° S. in a 2 dm tube); in glacial acetic acid $[\alpha]_D^{20} = +18.8$ (0.3055 g of the substance dissolved in 10 ml, six minutes after solution, read +3.31° S. in a 2 dm tube). The optical rotations of the solutions just given were read at intervals during the ensuing 24 hours and no changes were detected. However, in pyridine solution a small change was observed. The sample (0.2338 g) was dissolved in sufficient pyridine to give 10 ml of solution. The following specific rotations were obtained: +10.7, +10.5, +8.5, and +8.3, after 4, 60, 1,500 and 3,000 minutes, respectively. Analysis calculated for $C_{24}H_{34}O_{17}$: C, 48.46; H, 5.77. Found: C, 48.50; H, 5.74.

A methoxyl determination by Zeisel's method did not give any silver iodide; hence the substance does not contain a methoxyl group.

It gave essentially the same acetyl value when hydrolyzed with acids as with alkalies. The compound (0.2698 g) was refluxed with 50 ml of 0.2 *N* hydrochloric acid. The quantity of acetic acid which was liberated was equivalent to 27.20 ml of 0.1 *N* solution; the theoretical amount of acetic acid which could be derived from the sample or hexa-acetyl-4-glucosido-mannose is 27.24 ml of 0.1 solution. The alkaline hydrolysis was conducted in aqueous acetone solution. The sample (0.2330 g) was dissolved in about 10 ml of acetone and 30 ml of 0.1 *N* NaOH added. The solution was allowed to stand about two hours at room temperature. It was then titrated with standard acid. The titration showed that 23.33 ml of 0.1 *N* alkali had been neutralized; the theoretical amount of alkali which would be required for the saponification of six acetyl groups in the sample, is 23.5 ml of 0.1 *N* solution.

On acetylation with acetic anhydride and pyridine, hexa-acetyl-4-glucosido-mannose gives the previously known α-octa-acetyl-4-glucosido-mannose. The sample (0.5 g) of hexa-acetyl-4-glucosido-mannose was added to a cold ($-10°$ C.) mixture of acetic anhydride (7.5 ml) and pyridine (5 ml). The mixture was shaken until solution was complete and allowed to stand 18 hours at 0° C. It was then poured into ice water, and the product separated in the customary manner. The yield of pure octa-acetyl-4-glucosido-mannose was 0.5 g. It melted at 203° and gave $[\alpha]_D^{20} = +36.2$. These values are in agreement with properties of octa-acetyl-4-glucosido-mannose as reported by Brauns.[30]

6. PREPARATION OF CHLORO-HEPTA-ACETYL-4-GLUCOSIDO-MANNOSE FROM HEPTA-ACETYL-4-GLUCOSIDO-γ-METHYL-MANNOSIDE

Two grams of hepta-acetyl-4-glucosido-γ-methyl-mannoside was dissolved in 20 ml of chloroform. The specific rotation was then -12.7. Upon the addition of 15 ml of chloroform containing 0.149 g of hydrogen chloride the specific rotation changed rapidly, becoming constant in six minutes, $[\alpha]_D^{20} = +29.8$. After 15 minutes the solution was washed in a separatory funnel with ice water, followed by a cold dilute solution of sodium bicarbonate, and again with ice water. After evaporation of the dry chloroform solution chloro-hepta-acetyl-4-glucosido-mannose was obtained in the crystalline state. The crystals were washed with dry ether and then recrystallized from ethyl acetate by the addition of petroleum ether. About 1.3 g of the product was obtained. The recrystallized substance melted at 168° and gave $[\alpha]_D^{20} = +50.4$ (0.4605 g dissolved in 20 ml of chloroform read 6.7° S. in a 2 dm tube). According to Brauns chloro-hepta-acetyl-4-glucosido-mannose melts at 172° and gives $[\alpha]_D^{20} = +51.2$. Analysis calculated for $C_{26}H_{35}O_{17}Cl$: Cl, 5.42. Found: Cl, 5.35.

Chloro-hepta-acetyl-4-glucosido-mannose was also obtained by the use of titanium tetrachloride. A solution of 1.2 g of anhydrous titanium tetrachloride in 20 ml of chloroform was added to 4 g of hepta-acetyl-4-glucosido-γ-methyl-mannoside dissolved in 50 ml of chloroform. After refluxing four hours the cold chloroform solution was successively washed with ice water, dilute sodium bicarbonate solution and ice water. It was then dried with sodium sulphate and finally evaporated in vacuo. About 3.8 g of crystalline product was obtained. After recrystallization from ethyl acetate it melted at

[30] Brauns, J. Am. Chem. Soc., vol. 48, p. 2784; 1926.

169° and gave in chloroform solution $[\alpha]_D^{20} = +50.1$ (0.6080 g of substance dissolved in 20 ml of solution read 8.8° S. in a 2 dm tube). These properties indicate that the substance is chloro-hepta-acetyl-4-glucosido-mannose. Analysis calculated for $C_{26}H_{35}O_{17}Cl$: Cl, 5.42. Found: Cl, 5.29.

7. HEPTA-ACETYL-4-GLUCOSIDO-MANNOSE

Two grams of bromo-hepta-acetyl-4-glucosido-mannose was added to 50 ml of cold (−10° C.) acetone containing 5 ml of water and 5 g of silver carbonate. The mixture was shaken until all the bromine was converted into silver bromide, which was separated by filtration. The solution was allowed to evaporate spontaneously in an open beaker. Slender prismatic, needlelike crystals separated during the course of several hours. The crystals were collected upon a filter and washed with water. After drying at 50° in vacuo the substance weighed 1.5 g and melted at 105° to 110°. After recrystallization from hot water, in which it is difficultly soluble, it melted at 110°. Although the new substance is very soluble in ethyl acetate, chloroform, ether, and alcohol, it does not crystallize well from these solvents.

The optical rotation was determined in chloroform, methyl alcohol, and pyridine solutions. The recrystallized compound gave in chloroform, $[\alpha]_D^{20} = +11.7$ (1.3183 g of the substance dissolved in 25 ml read 3.56° S. in a 2 dm tube); in methyl alcohol, $[\alpha]_D^{20} = +11.6$ (0.4117 g of the substance dissolved in 25 ml, five minutes after solution, read 1.10° S. in a 2 dm tube). The optical rotations of the solutions just given were read at intervals during the day and no changes were detected. However, in pyridine solution a slow mutarotation was observed. The sample (0.2776 g) was dissolved in sufficient pyridine to give 10 ml of solution and the optical rotation was followed in a 2 dm tube with a Bates saccharimeter. $[\alpha]_D^{20} = +4.0$, $+4.6$, $+5.9$, $+6.9$, $+9.0$, and $+11.7$ after 0.1, 0.5, 2.0, 4.0, 10.0, and 60.0 hours, respectively; the rotation was virtually constant after 60 hours. Analysis calculated for $C_{26}H_{36}O_{18}$: C, 49.03; H, 5.70. Found: C, 48.70; H, 5.82.

A sample of the compound (0.1770 g) was refluxed four hours with 50 ml of 0.25 *N* sulphuric acid. The back titration with standard alkali gave a value equivalent to an increase of 19.33 ml 0.1 *N* acid; the theoretical quantity which could be derived from the sample of hepta-acetyl-4-glucosido-mannose is 19.47 ml 0.1 *N* acid. On acetylation with pyridine and acetic anhydride it gives α-octa-acetyl-4-glucosido-mannose. The sample (1.5 g) of hepta-acetyl-4-glucosido-mannose was dissolved in a cold (−10°) mixture of 10 ml of pyridine and 10 ml of acetic anhydride. After standing overnight in the refrigerator, the mixture was poured into ice water. The product which separated after recrystallization from methyl alcohol weighed 1.2 g. The substance was α-octa-acetyl-4-glucosido-mannose, $[\alpha]_D^{20} = +36$. The mother liquor gave 0.17 g of crude crystalline material which melted at 160° and gave $[\alpha]_D^{20} = +1.0$. The fact that α-octa-acetyl-4-glucosido-mannose is obtained in good yield on acetylation under the conditions just given indicates that the new compound is largely the alpha form of hepta-acetyl-4-glucosido-mannose. The explanation for the slight mutarotation in pyridine from a less dextro to a more dextro rotation must await further experimental study.

8. 4-GLUCOSIDO-β-MANNOSE

Crystalline 4-glucosido-β-mannose was prepared for the first time and its mutarotation measured. Five grams of 4-glucosido-α-mannose monohydrate was dissolved in about 150 ml of hot c. p. methyl alcohol. The mixture was warmed on the steam bath for about 30 minutes, and then it was allowed to cool slowly. On standing, crystallization occurred. Two types of crystals were observed. One of these is the anhydrous alpha form of the sugar and the other the anhydrous beta form. The alpha isomer separates in parallelepipeds which frequently become truncated, while the beta separates in slender needlelike prisms. The crude product was crystallized by dissolving it in a very small quantity of water and then adding cold glacial acetic acid. About 1.5 g of the nearly pure substance crystallized from the solution. The crude product, after thorough washing with warm methyl alcohol, was immersed in methyl alcohol and allowed to stand in a tightly stoppered flask. After several days the product was separated by filtration, washed with methyl alcohol, and dried at 60° C. Although it did not melt very sharply, it appeared homogeneous, and subsequent preparations gave essentially the same properties. It melted at 203° to 205° with decomposition. Analysis calculated for $C_{12}H_{22}O_{11}$: C, 42.08; H, 6.48. Found: C, 42.14; H, 6.47. The optical rotation was measured at 20° C. A sample (0.8673 g) of the finely powdered 4-glucosido-β-mannose was weighed into a glass-stoppered flask and 24.8857 g of water was added from a pipette which had been calibrated and found to deliver that weight of water in 20 second. The sugar was completely dissolved in 10 seconds after the addition of the first drop of water. Time was measured from the moment it was believed that half of the sugar was dissolved (three seconds after adding the first drop of water).

The following saccharimeter readings were observed using a 2 dm water-jacketed tube: −1.04 (3 minutes); −0.98 (4 minutes), −0.88 (5 minutes), −0.43 (10 minutes), +0.12 (20 minutes), +0.97 (50 minutes), and +1.27 (equilibrium value). The density of the solution was 1.008. The following specific rotations are obtained from the figures: $[\alpha]_D^{20} = -6.5$ (extrapolated value to zero time), −5.3 (3 minutes), −5.0 (4 minutes), −4.5 (5 minutes), −2.2 (10 minutes), +0.6 (20 minutes), +4.9 (50 minutes), and +6.5 (equilibrium value). The initial rotation (−6.5) is of the same order as the value $[\alpha]_D^{20} = -1.0$ obtained by Haworth, Hirst, Streight, Thomas, and Webb [31] by indirect means. These investigators were unable to obtain the crystalline beta compound, but estimated its rotation by the solubility method of Hudson and Yanovsky.[32] The equilibrium rotation is in accord with the value (+5.88) previously reported for the monohydrate; the rotation for the monohydrate is equivalent to $[\alpha]_D^{20} = +6.2$ for the anhydrous sugar. This value is considerably less than the value (+12.5) reported by Haworth, Hirst, Streight, Thomas, and Webb.

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[31] See footnote 7, p. 1116. [32] Hudson and Yanovsky, J. Am. Chem. Soc., vol. 39, p. 1035; 1917.

9. β-OCTA-ACETYL-4-GLUCOSIDO-MANNOSE

A finely powdered sample (1.1 g) of 4-glucosido-β-mannose was shaken with a cold (0°) solution of 25 ml of pyridine and 30 ml of acetic anhydride. When solution was complete (eight hours) the reaction mixture was allowed to stand in the refrigerator. After two days the product was isolated by pouring the mixture into ice water and separating the crystalline material. The crude product weighed 1.85 g, melted at 155° to 160°, and gave $[\alpha]_D^{20} = +6.8$. This product consisted of a mixture of α- and β-octa-acetyl-4-glucosido-mannose. The separation of the two substances by fractional crystallization from the usual solvents is very difficult. It was found, however, that the alpha form may be separated after about three crystallizations from toluene. The impure beta form, which crystallizes from the mother liquors on evaporation, may be purified by several crystallizations from ethyl acetate by the addition of ether. The product so obtained gave $[\alpha]_D^{20} = -11.8$; after one additional crystallization, $[\alpha]_D^{20} = -13.04$; after two crystallizations, $[\alpha]_D^{20} = -12.96$. It melted sharply at 165°. Analysis calculated for $C_{28}H_{38}O_{19}$: C, 49.54; H, 5.65. Found: C, 49.54; H, 5.65.

V. ACKNOWLEDGMENT

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WASHINGTON, July 30, 1931.

THERMAL EXPANSION OF GASOLINES FROM 0° TO 30° C.[1]

By C. S. Cragoe and E. E. Hill

ABSTRACT

Measurements are reported on the thermal expansion of 9 straight-run gasolines, 16 cracked gasolines, 3 motor benzols, and 5 benzol blends, from 0° to 30° C. The results indicate that the thermal expansion of cracked gasolines and benzol blends is systematically greater than the values based on straight-run gasolines given in National Standard Petroleum Oil Tables, Bureau of Standards Circular No. 154. The results also indicate that corrections for thermal expansion of present-day motor fuels, including straight-run gasolines, cracked gasolines, and benzol blends, can be made more accurately, in general, from a knowledge of their distillation curves than from gravity determinations.

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I. INTRODUCTION

The standard unit used most extensively in this country for determining quantities of gasoline and other petroleum products in commerce, is the gallon defined as 231 cubic inches of liquid at 60° F. In large-quantity shipments, tank cars for example, it is customary to determine the volume of gasoline at the existing temperature and to reduce the observed volume to the equivalent volume at 60° F. by the use of certain volume correction factors, such as those given in National Standard Petroleum Oil Tables, Bureau of Standards Circular No. 154.

The data on gasolines given in these tables are based upon measurements made prior to 1916 on the thermal expansion of straight-run gasolines, the only type of motor fuel in general use at that time. Approximately 50 per cent of the motor fuels now marketed consist of cracked gasolines and mixtures with benzol. Although the data given in Circular No. 154 were intended to be applicable only to straight-run gasolines, the data have been applied to cracked gasolines and benzol blends in the absence of definite information on these products. The work described in this paper was undertaken for the purpose of supplying experimental data on the thermal expansion of present-day motor fuels.

II. MATERIAL

The samples of gasolines and motor benzol used in this investigation, the information relating to their sources and the cracking processes used, were supplied for the most part by various oil companies through the courtesy of the American Petroleum Institute. A few of the gasoline samples were of unknown origin, having been submitted to the bureau for special tests.

[1] This paper contains results obtained in an investigation of the "Thermodynamic Properties of Petroleum Hydrocarbons" listed as Project No. 38 of the American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by John D. Rockefeller. This fund is being administered by the institute with the cooperation of the Central Petroleum Committee of the National Research Council.

Many of the cracked gasolines were not intended to be strictly representative of the marketed products, since some of the samples submitted were taken directly from the cracking units and other samples had been treated to remove certain undesirable constituents but had not been blended with natural gasoline. It is assumed, however, that the thermal expansion data herein reported are reasonably representative of the expansion of motor fuels in general.

III. APPARATUS AND METHODS

The apparatus and methods used in this work are essentially the same as those previously described in detail in publications [2] of this bureau.

The method of hydrostatic weighing was employed in most of the measurements. A sinker was weighed in the sample under investigation and the density of the sample was calculated from the known external volume of the sinker and the difference between its weight in vacuo and when immersed in the sample.

The familiar picnometer method was used with a few of the more volatile samples because the excessive evaporation loss at the higher temperatures limited very materially the accuracy attainable by the sinker method.

The thermostated bath used consists of a large Dewar flask which is equipped with a refrigerating brine coil, an electric heater and a mechanical stirring device. Two mercury-in-glass thermometers, which had been calibrated at this bureau, were used in all of the measurements.

IV. PROCEDURE AND CALCULATION

The density of each gasoline was determined at three temperatures, approximately 0°, 15.56°, and 30° C. Measurements were then repeated in the reverse order on another sample of the same material. An illustration of the quantities actually observed and the method of calculating the results is given in Table 1, which is typical of many such record sheets.

A sample of gasoline was placed in a special glass tube and immersed in the bath. The temperature of the bath was then brought to the desired point and maintained constant for about 20 minutes before observations were begun. The rate of cooling obtainable with the brine system employed was considerably less than the rate used in heating electrically. Thus, the second sample was at the higher temperatures for a longer time, affording greater opportunity for loss by evaporation. As a consequence, the observed density at the next lower temperature was somewhat too large and the apparent change in density of the second sample was found to be larger, in general, than that obtained on the first sample. Since the effect of evaporation loss is in the opposite direction in the case of the first sample, the mean of the four values obtained as shown in Table 1 was taken as the average change in density per degree. The average coefficient of expansion was calculated from this value by means of the relation

$$\text{Coefficient of expansion} = \frac{1}{V_{15.56}} \frac{\Delta V}{\Delta T} = -\frac{1}{D_{15.56}} \frac{\Delta D}{\Delta T}$$

[2] Bureau of Standards Bulletin, vol. 9, p. 371; 1913; and B. S. Tech. Paper No. 77.

TABLE 1.—*Sample records of observations and calculation of density by method of hydrostatic weighing*

(Sample, cracked gasoline from California)

FIRST SAMPLE

Observed temperature, thermometer No.—		Corrections to thermometers		Corrected temperature		Mean temperature t'	Balance reading	Apparent weight of sinker in liquid	Buoyancy correction on weights	True weight of sinker in liquid	Weight of displaced liquid	Volume of sinker at temperature t'	Density of liquid at t'/4°C.	Correction to integral degrees	Density of liquid at t/4°C.	Integral temperature t	Average density change per °C.
33557	33558																
°C.	°C.	°C.	°C.	°C.	°C.	°C.	g	g	g	g	g	ml	g/ml	g/ml	g/ml	°C.	g/ml °C.
							24.1125	62.7821									
0.09	0.09	−0.07	−0.06	0.02	0.03		86.8946	62.7832									
.08	.08			.01	.02	0.02	24.1114	62.7826	−0.0087	62.7739	37.1874	47.68818	0.779803	+0.000016	0.779819	0	
							23.4864	63.3751									0.000816
15.64	15.63	−.07	−.04	15.57	15.59		86.8615	63.3725									
15.62	15.58			15.55	15.54	15.56	23.4890	63.3738	−.0088	63.3650	36.5963	47.70619	.767118	.000000	.767118	15.56	
							22.9062	63.9248									0.000817
30.06	30.04	−.07	−.06	29.99	29.98		86.8310	63.9220									
30.07	30.05			30.00	29.99	29.99	22.9090	63.9234	−.0088	63.9146	36.0467	47.72266	.755337	−.000008	.755329	30	
SECOND SAMPLE																	
							22.9170	63.9145									
30.05	30.03	−0.07	−0.06	29.98	29.97		86.8315	63.9119									
30.07	30.05			30.00	29.99	29.99	22.9196	63.9132	−0.0088	63.9044	36.0569	47.72266	0.755551	−0.000008	0.755543	30	
							23.5125	63.3506									0.000834
15.61	15.57	−.07	−.04	15.54	15.53		86.8631	63.3491									
15.58	15.55			15.51	15.51	15.52	23.5140	63.3498	−.0088	63.3410	36.6203	47.70615	.767622	−.000033	.767589	15.56	
							24.1435	62.7529									0.000825
.08	.07	−.07	−.06	.01	.01		86.8964	62.7524									
.07	.06			0.00	0.00	0.00	24.1440	62.7527	−.0087	62.7440	37.2173	47.68816	.780431	.000000	.780431	0	
																Mean=	0.000823

Mass of sinker No. 7=99.9613 g. Buoyancy constant=1.025. Air density=0.001163 g/ml.

V. RESULTS

A summary of the results obtained on straight-run and cracked gasolines is given in Table 2, together with corresponding values of density change and coefficient of expansion used in the compilation of Circular No. 154. Table 3 gives a similar summary of the results obtained on three motor benzols from different sources and several specially prepared mixtures of straight-run gasoline and motor benzol. The distillation data, given in Table 4, were obtained using A. S. T. M.[a] Standard Method D86.

TABLE 2.—*Data on thermal expansion of gasolines*

STRAIGHT-RUN GASOLINES

Sample No.	Sample derived from oil from—	Cracking process used	Specific gravity at 60°/60° F.	Degrees A. P. I.	Density change per ° F.		Coefficient of expansion per ° F.	
					Observed	C. 154	Observed	C. 154
1	Pennsylvania		0.7494	57.32	0.00045	0.00045	0.00060	0.00060
2	West Virginia		.7273	63.06	.00046	.00047	.00063	.00064
3	do		.6950	72.10	.00049	.00049	.00070	.00071
4	Kansas		.7525	56.54	.00045	.00045	.00060	.00060
5	Oklahoma		.6970	71.51	.00050	.00049	.00072	.00071
6	Texas		.7488	57.47	.00046	.00045	.00061	.00060
7	California		.7581	55.15	.00046	.00044	.00061	.00058
8	do		.7618	54.24	.00046	.00044	.00061	.00058
9 [1]			.7841	48.96	.00042	.00042	.00054	.00053

LIQUID-PHASE CRACKED GASOLINES

10	Pennsylvania	Dubbs	0.7386	60.08	0.00048	0.00046	0.00064	0.00062
11 [2]	do	Cross	.7417	59.28	.00047	.00045	.00063	.00061
12 [3]	Mid-Continent	Holmes-Manley	.7415	59.33	.00047	.00045	.00063	.00061
13	do	Tank and tube	.7399	59.74	.00047	.00046	.00063	.00062
14 [4]	Mixture from Oklahoma, Texas, Louisiana and Gulf Coast	Cross	.7453	58.36	.00047	.00045	.00063	.00061
15 [5]		do	.7537	56.24	.00046	.00044	.00062	.00059
16 [6]	Panhandle	Dubbs	.7525	56.54	.00047	.00045	.00062	.00060
17 [4]	Kansas	do	.7404	59.61	.00048	.00046	.00064	.00062
18 [4]	Oklahoma	Cross	.7584	55.08	.00046	.00044	.00061	.00058
19 [3]	do	Dubbs	.7230	64.21	.00048	.00047	.00067	.00065
20	Texas	Holmes-Manley	.7523	56.59	.00046	.00045	.00061	.00060
21 [6]	California	Doherty	.7582	55.13	.00047	.00044	.00061	.00058
22	do	Cross	.7681	52.72	.00046	.00044	.00059	.00057

VAPOR-PHASE CRACKED GASOLINES

23	West Virginia	Gyro	0.7436	58.79	0.00047	0.00045	0.00064	0.00061
24 [7]			.7769	50.63	.00047	.00043	.00060	.00055
25			.7797	49.98	.00046	.00042	.00059	.00054

[1] Mineral spirits used as a paint thinner and also as a damping liquid in aircraft compasses. (For specification, see B. S. Circular No. 98.)
[2] Before blending.
[3] Treated and redistilled.
[4] Direct from cracking unit.
[5] After treating.
[6] Before treating.
[7] Cracking process used is described in National Petroleum News, vol. 18, p. 104; 1926.

[a] Proceedings of the American Society for Testing Materials, vol. 26, p. 816; 1926.

TABLE 3.—*Data on thermal expansion of motor benzols and gasoline-benzol blends*

Sample No.	Percentage by volume		Specific gravity 60°/60° F.	Degrees A. P. I.	Density change per ° F.			Coefficient of expansion per ° F.		
	A	B			Observed	Calculated [1]	Circular 154 [2]	Observed	Calculated [1]	Circular 154 [2]
4	0	[3] 100	0.7525	56.54	0.00045		0.00045	0.00060		0.00060
26	10	90	.7647	53.54	.00046	0.00046	.00044	.00060	0.00060	.00057
27	25	75	.7825	49.33	.00048	.00048	.00041	.00061	.00061	.00053
28	50	50	.8138	42.37	.00051	.00051	.00040	.00063	.00063	.00049
33	[4] 100	0	.8824	28.86	.00058		.00037	.00066		.00042
2	0	[5] 100	.7275	63.00	.00046		.00047	.00063		.00064
29	25	75	.7640	53.71	.00048	.00048	.00044	.00063	.00063	.00057
30	50	50	.8005	45.26	.00050	.00051	.00040	.00063	.00064	.00050
31	[6] 100	0	.8793	29.42	.00056		.00037	.00064		.00042
32	[7] 100	0	.8772	29.81	.00057		.00037	.00065		.00042

[1] See Section VII for method of calculation.
[2] These values are given here for the purpose of comparison only. The data in Circular No. 154 were not intended to be applicable to motor benzol or to gasoline-benzol blends.
[3] Straight-run gasoline obtained from Kansas crude.
[4] Motor benzol obtained from Gary, Ind.
[5] Straight-run gasoline obtained from West Virginia crude.
[6] Motor benzol obtained from Lackawanna, Pa.
[7] Motor benzol obtained from Woodlawn, Pa.

TABLE 4.—*Distillation data*

STRAIGHT-RUN GASOLINES

Sample No.	Temperature in ° C. at various percentages distilled—											Residue	Loss	Average volatility
	Initial	10	20	30	40	50	60	70	80	90	End			
												Per cent	*Per cent*	° *C.*
1	55	87	100	112	123	134	146	160	174	190	218	1.2	1.2	136
2	40	70	85	98	110	122	134	148	165	185	216	1.4	1.3	124
3	53	------	75	------	------	79	------	------	------	110	163	1.8	0.4	[1] 87
4	48	80	96	110	122	134	146	159	173	189	206	1.2	1.6	132
5	58	------	68	------	------	72	------	------	------	85	106	0.5	0.5	[1] 75
6	50	74	87	100	113	125	138	152	167	183	204	1.2	1.4	125
7	50	78	96	109	122	134	148	162	178	198	220	1.4	1.1	135
8	52	78	95	109	122	135	149	164	180	200	220	1.2	0.8	136
9	158	162	165	168	171	174	177	180	184	193	210	1.7	0.3	176
CRACKED GASOLINES														
10	35	60	74	87	102	118	134	150	169	189	215	1.0	2.2	119
11	40	65	79	92	116	130	146	163	180	196	210	1.1	2.1	128
12	40	66	85	99	112	123	135	150	166	184	218	1.2	1.8	121
13	39	65	83	98	112	126	140	155	170	186	196	0.9	1.7	123
14	28	56	76	94	111	127	144	162	180	198	212	1.0	4.6	119
15	40	68	88	105	121	135	150	165	180	196	207	0.9	1.8	130
16	40	66	85	102	118	132	147	162	178	196	219	1.1	1.7	129
17	29	56	72	85	98	111	125	141	160	182	213	1.3	2.7	112
18	42	67	86	103	118	133	149	166	184	203	217	1.2	1.5	132
19	40	60	74	86	98	109	120	132	144	156	169	1.1	1.4	107
20	48	73	93	109	124	138	152	167	182	197	212	1.6	1.4	134
21	38	63	82	99	114	129	145	152	170	190	209	1.2	1.8	124
22	40	69	89	107	124	140	157	174	192	202	222	1.2	1.8	133

[1] Estimated the 10 per cent point from curve.

TABLE 4.—*Distillation data*—Continued.

GASOLINE-BENZOL BLENDS

Sample No.	Temperature in ° C. at various percentages distilled—											Residue	Loss	Average volatility
	Initial	10	20	30	40	50	60	70	80	90	End			
												Per cent	*Per cent*	*° C.*
26	65	83	92	102	116	129	143	158	170	188	206	0.9	1.4	131
27	69	82	88	94	101	113	127	146	166	184	200	0.9	1.4	125
28	74	81	84	87	90	95	102	120	141	174	201	1.0	1.5	114
29	66	80	87	94	102	112	123	137	155	180	216	1.3	0.9	122
30	74	84	88	91	95	100	110	124	146	175	208	1.1	0.9	118
MOTOR BENZOLS														
31	82	85	86	87	88	90	92	95	103	119	146	1.0	0.7	98
32	75	82	85	85	85	86	87	89	96	118	144	0.6	0.9	95
33	79	81	82	82	83	84	84	85	88	100	145	0.4	1.0	88

VI. VOLUME AND TEMPERATURE CHANGES ON MIXING GASOLINE AND BENZOL

It is well known that appreciable changes in volume and temperature accompany the mixing of certain liquids, a familiar example being water and alcohol. Such changes are usually considered to be very small, however, in the blending of petroleum oils.

In the preparation of definite mixtures of gasoline and motor benzol relatively large temperature changes were noted and it appeared to be of some interest to measure with moderate accuracy the temperature and volume changes on mixing. Equal volumes of the two liquids were measured in separate calibrated flasks at approximately 25° C. The two liquids were then transferred to a larger flask of twice the capacity and the temperature observed after thorough mixing. The mixture was brought to the initial temperature and the increase in volume on mixing was observed. The results obtained are recorded in Table 5.

TABLE 5.—*Volume and temperature changes on mixing*

Sample No.	Material	Sample obtained from—	Temperature		Temperature change	Expansion	Percentage A by volume
			Before mixing	After mixing			
			° C	*° C*	*° C*	*Per cent*	
4	A Gasoline	Kansas crude	25.2	21.6	−3.6	+0.33	50
33	B Benzol	Gary, Ind.					
2	A Gasoline	West Virginia crude	24.9	21.5	−3.4	+.36	50
31	B Benzol	Lackawanna, Pa.					
8	A Gasoline	California	25.0	21.9	−3.1		50
32	B Benzol	Woodlawn, Pa.					

TABLE 5.—*Volume and temperature changes on mixing*—Continued

For the purpose of comparison, the following data on pure substances are quoted from Sidney Young, Fractional Distillation, p. 40 and p. 42, MacMillan & Co. (Ltd.), London, 1903

Sample No.	Material	Sample obtained from—	Temperature		Temperature change	Expansion	Percentage A molal
			Before mixing	After mixing			
					°C	*Per cent*	
	A Benzene				−4.7	+0.52	50
	B *n*-hexane						
	A *n*-hexane				+.06	−.053	50
	B *n*-octane						
	A Water				+2.95	−2.56	40
	B Ethyl alcohol						

The data obtained by Sidney Young on mixtures of benzene and *n*-hexane, quoted in this table, show changes in the same direction and of the same order of magnitude while the changes observed with mixtures of *n*-hexane—*n*-octane, and water-alcohol are in the opposite direction and of a different order of magnitude.

VII. CALCULATION OF EXPANSION OF BENZOL BLENDS BY MIXTURE RULES

Since the expansion on mixing gasoline and benzol is relatively small, approximate values for the density of known mixtures at a given temperature may be calculated from the relation

$$100\,D_m = xD_b + (100-x)D_g$$

in which the subscripts refer to mixture, benzol, and gasoline, respectively, D = density, and x = per cent benzol, by volume. By substituting in this relation, the general equation

$$D_t = D_o - \alpha\,(t-t_o)$$

in which t = temperature, α = change in density per degree at t_o, and the subscript zero refers to any convenient reference temperature, it follows that

$$100\alpha_m = x\alpha_b + (100-x)\alpha_g$$

Similarly, from the relation between coefficient of expansion and change in density per degree,

$$A = \frac{1}{V_o}\frac{dV}{dt} = -\frac{1}{D_o}\frac{dD}{dt} = \frac{\alpha}{D_o}$$

it follows that

$$100A_mD_m = xA_bD_b + (100-x)A_gD_g$$

Values calculated from these mixture rules are in good agreement with the observed values, as shown in Table 3. These mixture rules were used to calculate the tables on thermal expansion of gasoline-benzol mixtures and also the corrections to readings of hydrometers in such mixtures, given in Bureau of Standards, Miscellaneous Publica-

tion No. 97, Thermal Properties of Petroleum Products. The data herein reported on such mixtures constitute the experimental basis for those tables, which give values for mixtures containing 25 and 50 per cent benzol. The practical usefulness of the tables is rather limited, however, because the benzol content must be known in order to make accurate interpolation of the tabulated data. A more useful and accurate means of making corrections for thermal expansion is given later.

VIII. COMPARISON WITH PREVIOUS WORK

Table 6 gives data obtained by previous observers on presumably straight-run petroleum products which come within the gravity range covered in the present work. Figure 1 gives a graphical comparison of these data with the present results, Circular No. 154, and most of the available data on pure hydrocarbons of comparable gravity and volatility.

TABLE 6.—*Data of previous observers*

DATA OBTAINED BY H. W. BEARCE AND E. L. PEFFER, B. S. TECH. PAPER NO. 77; 1916

Nature of oil	Derived from oil from—	Specific gravity at 60°/60° F.	Degrees A. P. I.	Density change per ° F.		Coefficient of expansion per ° F.	
				Observed	Circular 154	Observed	Circular 154
Naphtha		0.6872	74.4	0.00049	0.00049	0.00072	0.00072
Gasoline		.7066	68.7	.00048	.00048	.00068	.00068
Naphtha		.7108	67.6	.00049	.00048	.00069	.00068
Gasoline	Texas	.7353	60.2	.00047	.00046	.00064	.00062
	Pennsylvania	.7394	59.9	.00046	.00046	.00062	.00062
	California	.7407	59.5	.00048	.00046	.00065	.00062
Benzine	do	.7517	56.7	.00047	.00044	.00063	.00059
Naphtha	Indiana	.7536	56.3	.00046	.00044	.00061	.00059
Engine distillate	California	.7762	50.8	.00044	.00043	.00057	.00055
Gasoline	Oklahoma	.7840	49.0	.00042	.00042	.00054	.00054

DATA OBTAINED BY ZEITFUCHS, INDUSTRIAL & ENGINEERING CHEMISTRY, VOL 17, P. 1280; 1925

Gasoline	California	0.7662	53.2	0.00048	0.00044	0.00062	0.00057
Crude naphtha	do	.7886	47.9	.00046	.00042	.00058	.00053
Engine distillate	do	.7991	45.6	.00047	.00041	.00059	.00051

Data are included on the following compounds: Paraffin series, normal compounds from C_7H_{16} to $C_{16}H_{34}$; naphthene series, the following monocyclics, cyclopentane, cyclohexane, cycloheptane and cyclooctane and the following substituted monocyclics, methylcyclopentane, methylcyclohexane, ethylcyclobutane, 1–1 and 1–4 dimethylcyclohexane; aromatic series, benzene, toluene, *m*-xylene, and *n*-propylbenzene. The data on these compounds were taken from the following sources: International Critical Tables, Vol. III; Engler-Hofer, Das Erdol. Vol. I; and Beilstein Vol. V. While there may be some question relative to the accuracy of the data on these hydrocarbons and also to their purity, the data serve a useful purpose here, however, to indicate trends.

The data presented in Figure 1 indicate that the results obtained on motor fuels are consistent, in general, with available information on their composition. Straight-run gasolines from eastern and mid-

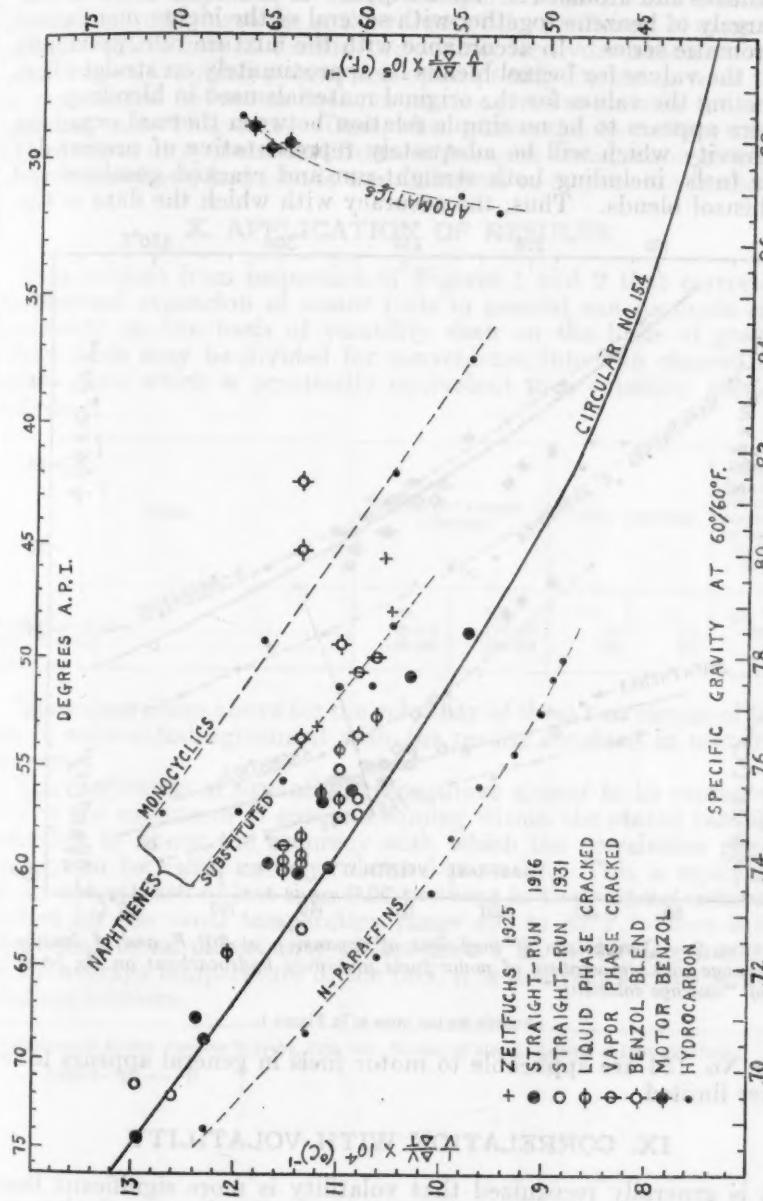

FIGURE 1—*Comparison of coefficient of expansion at 60° F. of motor fuels and pure hydrocarbons on the basis of gravity*

continent crudes, for example, are known to be rich in paraffin series hydrocarbons, while straight-run gasolines from many California crudes and also cracked gasolines are known to be relatively richer in naphthenes and aromatics. Similarly, motor benzol is known to consist largely of benzene together with several of the higher members of the aromatic series. In accordance with the mixture rule, previously given, the values for benzol blends lie approximately on straight lines connecting the values for the original materials used in blending.

There appears to be no simple relation between thermal expansion and gravity which will be adequately representative of present-day motor fuels, including both straight-run and cracked gasolines and also benzol blends. Thus, the accuracy with which the data in Cir-

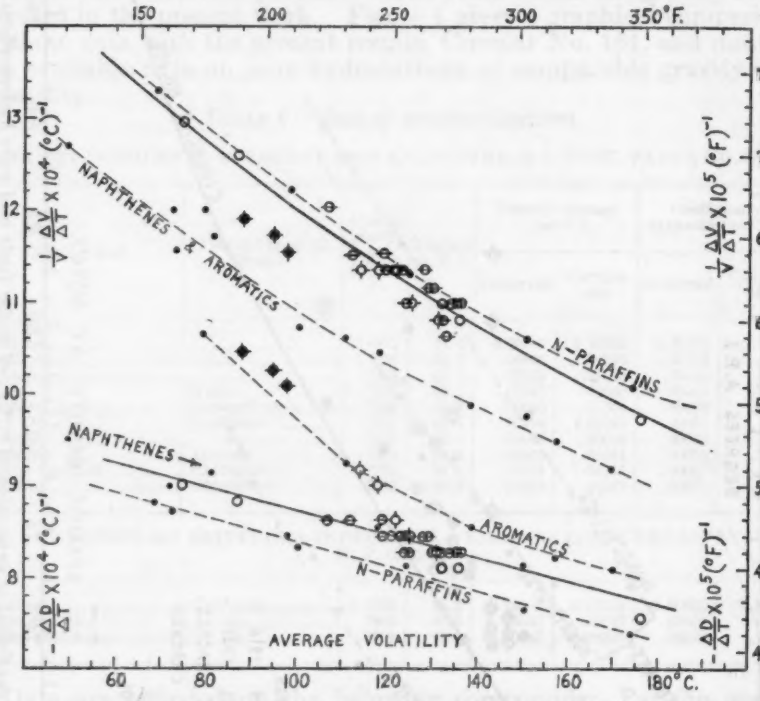

FIGURE 2.—*Comparison of coefficient of expansion at 60° F. and of density change with temperature of motor fuels and pure hydrocarbons on the basis of "average volatility"*

Symbols are the same as in Figure 1.

cular No. 154 are applicable to motor fuels in general appears to be rather limited.

IX. CORRELATION WITH VOLATILITY

It is generally recognized that volatility is more significant than gravity as an index of the suitability of a gasoline for a particular use. Most specifications, for example, require a distillation test, whereas a gravity determination is not required. It appears also from the results reported herein that "average volatility" serves much better than gravity as an index of thermal expansion. "Average volatility"

as used here is defined as the average of the temperatures at which 10, 50, and 90 per cent is evaporated. (Per cent evaporated = per cent distilled plus evaporation loss.)

As shown in Figure 2, in which the symbols are the same as those used in Figure 1, the range in the values of the coefficient of expansion and also the change in density per degree, for hydrocarbons of comparable normal boiling points, and consequently for mixtures of them as represented by motor fuels, is much narrower than in the corresponding case of Figure 1. Thus, when put on this basis there appear to be little or no systematic differences between straight-run gasolines, cracked gasolines, and blends containing up to 50 per cent benzol.

X. APPLICATION OF RESULTS

It is evident from inspection of Figures 1 and 2 that corrections for thermal expansion of motor fuels in general can be made more accurately on the basis of volatility than on the basis of gravity. Motor fuels may be divided for convenience into two classes, on a utility basis which is practically equivalent to a volatility basis, as follows:

Class	Range of "average volatility"		Mean volatility		Corresponding average coefficient of expansion at 60° F
	°C.	°F.	°C.	°F.	per °F.
Aviation gasoline	80–110	176–230	95	203	0.00068
Motor gasoline	110–140	230–284	125	257	.00062

The values given above for the volatility of these two classes of fuels are in substantial agreement with the results obtained in numerous surveys.[4]

The coefficients of expansion given above appear to be representative of the expansion of gasoline coming within the stated ranges of volatility to about the accuracy with which the correlation (fig. 2) appears to be valid, namely, about 5 per cent. This is equivalent to an uncertainty of less than 0.07 per cent in the volume correction factors for the usual temperature range 40° to 80°F. Since this is equivalent to an uncertainty of less than 1°F. in the determination of the average temperature of the fuel, it is not very serious in practical applications.

[4] Semiannual Motor Gasoline Surveys, 1920-1931, Bureau of Mines, Reports of Investigations.

TABLE 7—*Volume correction factors for gasolines*

Observed temperature, ° F.	Volume at 60° F. occupied by unit volume at observed temperature		Observed temperature, ° F.	Volume at 60° F. occupied by unit volume at observed temperature	
	Aviation gasolines	Motor gasolines		Aviation gasolines	Motor gasolines
	"Average volatility"			"Average volatility"	
	80°-110° C. 176°-230° F.	110°-140° C. 230°-284° F.		80°-110° C. 176°-230° F.	110°-140° C. 230°-284° F.
0	1.0407	1.0370	60	1.0000	1.0000
1	1.0400	1.0364	61	.9993	.9994
2	1.0393	1.0358	62	.9986	.9988
3	1.0387	1.0351	63	.9980	.9981
4	1.0380	1.0345	64	.9973	.9975
5	1.0373	1.0339	65	.9966	.9969
6	1.0366	1.0333	66	.9959	.9963
7	1.0359	1.0327	67	.9952	.9957
8	1.0353	1.0321	68	.9946	.9950
9	1.0346	1.0315	69	.9939	.9944
10	1.0339	1.0309	70	.9932	.9938
11	1.0332	1.0303	71	.9925	.9932
12	1.0326	1.0297	72	.9918	.9926
13	1.0319	1.0290	73	.9911	.9919
14	1.0313	1.0284	74	.9904	.9913
15	1.0306	1.0278	75	.9897	.9907
16	1.0299	1.0272	76	.9890	.9901
17	1.0292	1.0266	77	.9883	.9895
18	1.0286	1.0259	78	.9877	.9888
19	1.0279	1.0253	79	.9870	.9882
20	1.0272	1.0247	80	.9863	.9876
21	1.0265	1.0241	81	.9856	.9870
22	1.0258	1.0235	82	.9849	.9863
23	1.0252	1.0229	83	.9842	.9857
24	1.0245	1.0223	84	.9835	.9850
25	1.0238	1.0217	85	.9828	.9844
26	1.0231	1.0211	86	.9821	.9838
27	1.0225	1.0205	87	.9814	.9832
28	1.0218	1.0198	88	.9808	.9825
29	1.0212	1.0192	89	.9801	.9819
30	1.0205	1.0186	90	.9794	.9813
31	1.0198	1.0180	91	.9787	.9807
32	1.0191	1.0174	92	.9780	.9801
33	1.0184	1.0167	93	.9774	.9794
34	1.0177	1.0161	94	.9767	.9788
35	1.0170	1.0155	95	.9760	.9782
36	1.0163	1.0149	96	.9753	.9776
37	1.0156	1.0143	97	.9746	.9770
38	1.0150	1.0136	98	.9739	.9763
39	1.0143	1.0130	99	.9732	.9757
40	1.0136	1.0124	100	.9725	.9751
41	1.0129	1.0118	101	.9718	.9745
42	1.0123	1.0112	102	.9711	.9739
43	1.0116	1.0105	103	.9705	.9732
44	1.0110	1.0099	104	.9698	.9726
45	1.0103	1.0093	105	.9691	.9720
46	1.0096	1.0087	106	.9684	.9714
47	1.0089	1.0081	107	.9677	.9708
48	1.0082	1.0074	108	.9670	.9701
49	1.0075	1.0068	109	.9663	.9695
50	1.0068	1.0062	110	.9656	.9689
51	1.0061	1.0056	111	.9649	.9683
52	1.0054	1.0050	112	.9642	.9676
53	1.0048	1.0043	113	.9635	.9670
54	1.0041	1.0037	114	.9628	.9663
55	1.0034	1.0031	115	.9621	.9657
56	1.0027	1.0025	116	.9614	.9651
57	1.0020	1.0019	117	.9607	.9645
58	1.0014	1.0012	118	.9601	.9638
59	1.0007	1.0006	119	.9594	.9632
60	1.0000	1.0000	120	.9587	.9626

Volume correction factors, based upon the above coefficients of expansion, are given in Table 7. The data in this table furnish a convenient and accurate means for reducing volumes of gasoline to the basis of 60° F. The factors given in this table are in the form of "multipliers"; that is, the observed volume of gasoline at the observed temperature, multiplied by the corresponding correction factor in the table, equals the volume at 60° F. For example, if the "average volatility" (which corresponds approximately to the 50 per cent point on the distillation curve) of the gasoline is within the range 230° to 284° F. (110° to 140° C.) and the observed volume at 90° F. is 10,000 gallons, then the volume at 60° F. equals $10,000 \times 0.9813 = 9,813$ gallons.

WASHINGTON, September 15, 1931.

TESTS OF INTEGRAL AND SURFACE WATERPROOFINGS FOR CONCRETE

By C. H. Jumper

ABSTRACT

The paper is a report of the study of integral and surface waterproofing materials for concrete.

Fifty commercial integral waterproofing materials were incorporated into a 1:3:6 concrete and subjected to a water pressure of 20 lbs./in.^{2} for one year and their permeability noted in comparison with plain concrete of the same quality tested in a similar manner. Strength and absorption results were also obtained. The materials are grouped in accordance with their chemical composition and a detailed discussion is given of the effect of each material on concrete as well as a general summary of the effects of each group.

The 50 surface waterproofing materials were applied to 3 by 6 inch concrete cylinders and their absorption determined, after immersion in water, at regular intervals up to one year. A comparison of these results with the absorption figures obtained on uncoated concrete, given the same treatment, are presented and discussed. A general résumé is given of the results obtained in the study of integral and surface waterproofings.

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I. INTRODUCTION

The introduction and sale of a large number of newly named integral and surface waterproofing materials for concrete has resulted in frequent requests to the bureau by the several departments of the Government and by the public for information regarding the relative merits of these compounds. The bureau has, therefore, felt the necessity of supplementing the work published in Technologic Paper No. 3 of the bureau in 1911, inasmuch as it is possible that since the issuing of that publication some of the products on the market may be new compounds not included in the former work or that some of the older ones may have been improved.

In this investigation, it was first necessary to develop a concrete that when subjected to a water pressure of 20 lbs./in.^{2} would be permeable to a slight extent, and could be duplicated so as to give reasonably consistent results. Laboratory-made specimens of what would generally be called poor concrete invariably showed no or erratic permeability. Several hundred specimens were made using mixes of concretes varying from 1:1:5 to 1:4:6. The water-cement ratio and the grading of sand and gravel were varied for each of the mixes. The tests on these several mixes showed that a mix of dry consistency was too permeable and a mix that was wet enough to be workable was practically impervious. The medium flow between a dry mix and a workable mix, that would allow a small amount of water to pass through the specimen, could not be obtained on mixes that are commonly used. For example, in trying to design a 1:2:4 mix that would be permeable to a slight extent, the grading of sand and gravel were kept constant and the water-cement ratio was varied from 0.72 to 0.75 and 0.79. The specimens with a water-cement ratio of 0.72 were quite permeable and the results quite inconsistent, but the specimens with a water-cement ratio of 0.75 and 0.79 were impermeable. It seemed practically impossible to make a 1:2:4 mix that was just dry enough or just wet enough to give a concrete that was just slightly permeable and, therefore, might be rendered less pervious through the addition of the waterproofing and that could be duplicated. As a result of considerable experimentation, a 1:3:6 mix by volume was finally adopted as best meeting the laboratory requirements.

II. METHOD OF FABRICATION OF INTEGRAL TEST SPECIMENS

1. PERMEABILITY SPECIMENS

Portland cement, complying with the standards of the United States Government, Potomac River sand and a gravel graded between No. 4 to ¾ inch, were used in all test specimens. The grading analysis of the Potomac River sand gave the following percentages retained on the sieves: No. 4 sieve 3, No. 8 sieve 18, No. 16 sieve 32, No. 30 sieve 60, No. 50 sieve 97, and No. 100 sieve 99.

Sufficient materials to make five test specimens were placed in a large galvanized-iron pan and thoroughly dry mixed. Water was then added to give a water-cement ratio of 1.26 by volume. The mixing was continued for two minutes by hand. The concrete was then placed in five metal cyclinders 5 inches in diameter and 5 inches

high by pouring through a cone containing baffles. This served to break up the mix and give an even distribution over the area of the mold. The mix was placed in three layers, each layer was stirred just sufficiently with an iron stirring rod to assist in distributing the concrete evenly over the mold. No tamping was done. After the concrete was placed in the molds, an outside cylinder of galvanized iron, 7 inches in diameter and 2 inches high, was placed around each mold and the 1-inch space was filled with a fairly wet 1:2 mix of cement and sand.

The inside 5-inch mold was then carefully withdrawn so as not to disturb the concrete mix. The outside mold was allowed to remain permanently around the concrete. The five spec mens were then securely held to the top of a flow table to prevent sliding and given 30 one-eighth inch drops. This caused the concrete to be compacted and produced a bond between the concrete and the outside layer of mortar. The surplus concrete was then struck off with a trowel and the specimens were removed to a laboratory table and covered with steel plates. After 24 hours the plates were removed and the concrete surfaces were wire-brushed to remove all neat cement that might have come to the top or settled to the bottom.

A neat cement cap approximately one-eighth inch thick was spread over the 1-inch mortar surface surrounding the 5-inch diameter specimen. The test pieces were then placed in the damp closet for 24 hours after which the neat cement caps were scraped to a smooth surface. The specimens were then allowed to remain in the damp closet until seven days old. All operations were conducted in a constant temperature room maintained at 70° F. ± 3°.

The integral waterproofing materials were supplied either as a powder, paste, or liquid. The powders were added directly to the dry mix and thoroughly incorporated in the mix before the water was added. The paste and liquid waterproofing compounds were added to the mixing water. In all cases the directions for mixing and the amount to be used per bag of cement as furnished by the manufacturer were carefully complied with.

In addition to making the 50 batches, each containing one of the 50 integral waterproofing compounds, 6 batches were made in the same manner without the addition of compounds and were used as a basis for comparison for determining the efficiency of the waterproofing compounds.

2. STRENGTH AND ABSORPTION SPECIMENS

Portland cement as used in the permeability specimens. Potomac River sand and No. 4 to ⅜-inch gravel were used. Sufficient materials to make twelve 3 by 6 inch cylinders, of a 1:3:6 mix by volume were placed in a large galvanized iron pan and thoroughly mixed by hand. Water was then added to give a concrete with a water-cement ratio of 1.26 by volume. After mixing for two minutes, the concrete was placed in the 3 by 6 inch cylinder molds in three layers, each layer being rodded 25 times. Nine cylinders from each batch were capped with neat cement and three to be used for the absorption tests struck off flush with the top of the mold.

The waterproofing agents were added to the concrete mixes in the amounts and manner suggested by each manufacturer. On several occasions concrete was made to which no waterproofing was added; the specimens so made served as "blanks."

III. METHOD OF TEST (INTEGRAL)

1. PERMEABILITY TESTS

After the curing period of seven days in the damp closet, the specimens to be tested for permeability were placed in the test piece holders. A holder consists of two cast-iron pipe flanges. The upper flange is closed with a pipe plug through which passes a ¼-inch pipe supplied with a union for attaching to the water line. The plug is also supplied with a ¼-inch petcock for venting the air at the time of starting the test. The lower flange is also closed with a pipe plug through which passes a ½-inch pipe to which a rubber hose is connected to deliver the water passing through the specimen to a measuring cylinder. Rubber gaskets are used between the test piece and the flanges. Eight bolts are used to draw the flanges together, thus making a tight seal so that no water can leak out between the flanges. The test piece after being securely fastened in the holder was placed on a rack and connected to the water line.

Water was supplied from the city main and was passed through a sand filter to remove all sediment. A control valve was placed in the line between the test specimens and the filter and a pressure of 20 pounds was maintained in the system at all times. The set up consisted of six racks that accommodated 36 specimens each.

The first determinations of the flow were taken 24 hours after the test specimens were placed under pressure and then daily until the twenty-eighth day. At the age of 28 days, three test specimens were selected from the five under test for each compound, which appeared to have uniform permeability and were representative of the compound. Observations were then taken each week, covering a period of one year, on the three test specimens.

At the end of the year period the test specimens were taken down and thoroughly wire-brushed to remove any rust or sediment that might have collected on the top of the specimen during the year exposure. They were again placed in the holders and the test continued for two months. Observations were made at regular intervals after the first 24 hours.

After this 2-month test the specimens were again taken down, removed from the holder, and allowed to dry in the air of the laboratory for one month. They were then placed under pressure and the permeability noted over a period of a month.

The average values, taken at regular intervals, of the amount of water passing through the three specimens of any one mix are reported in cubic centimeters per 100 square centimeters of surface per hour. These results are presented in the accompanying figures.

2. ABSORPTION TESTS

The absorption cylinders were cured in the damp closet for 19 days. They were then placed in an oven at 65° C., through which dry air was circulated to promote drying, and dried to constant weight.

At 28 days they were weighed, then immersed in water for one hour, then dried with a damp towel, weighed, and immersed again. This procedure was followed and the absorption determined at 1 hour, 2 hours, 4 hours, 24 hours, 48 hours, and 72 hours. They were then placed in the damp closet for one year. At the end of this period they were again dried to constant weight at 65° C. and the above procedure repeated.

The absorption was computed from the recorded weights, and is reported in per cent of the dry weight.

3. COMPRESSION TESTS

Three of the 3 by 6 inch cylinders from each of the 50 mixes containing waterproofing materials and three cylinders from several mixes containing no waterproofing or additive materials were tested in compression, after curing in the damp closet, at the age of 7 days, 28 days, and 1 year.

The compressive strength in pounds per square inch given in the table is the average of the three cylinders from each mix at each age.

IV. INTEGRAL WATERPROOFING MATERIALS

1. COMMERCIAL NAMES

The materials used in this investigation were furnished by the manufacturer under the following trade names:

A. B. Integral Hardner.
A. B. Waterproofing Powder.
Acqua-Pruf.
Adensite.
Alberoyd.
Alkalgel A.
Alkalgel B2.
Alkalgel B3.
Anti-Hydro.
Aquabar Aquatite Liquid.
B. C. C. Oil Waterproofing.
Biber A.
Butyl Stearate.
Cal.
Celite.
Ceresit Liquid.
Ceresit Paste. .
Ceresit Powder.
Colloy.
Con wat co Mix.
Dragon Super Cement.
Fluresit.
G. F. 10.
G. F. 12 Accelerator.
Hydratite Liquid.
Hydratite No. 4 Paste.
Hydrocide Paste.
Hydrocide Powder.
Konset.
Luigi Serra.
Master Builders Concentrated Liquid.
Master Builders New Master Mix.
Master Builders Paste.
Medusa Waterproofed Cement.
Medusa Waterproofing Powder.
Non-Poro.
Penetrite Paste.
Penetrite Powder.
Permantite.
Rubberoid Waterproofing Paste.
Se-Ment-Seal.
Sika No. 1.
Sulco Liquid.
Toxement Paste.
Toxement Powder.
Toxmix Clear.
Tricosal Normal.

In addition to these compounds a high calcium lime, a dolomitic lime, and potter's flint were included in the investigation.

2. COMPOSITION AND METHOD OF INCORPORATION

The waterproofings have been grouped in accordance with their chemical composition. The first group of waterproofings are those containing calcium chloride and water, the second contains calcium chloride with miscellaneous materials, the third soaps, the fourth hydrated lime with soaps, the fifth finely subdivided materials, and the sixth group miscellaneous materials. These waterproofing materials are briefly described in Table 1.

TABLE 1.—*Composition and method of incorporation of integral waterproofing materials*

Group No. 1. CALCIUM CHLORIDE

Material No.	Composition	Method of incorporation
24	Light yellow colored liquid with a small amount of flocculent precipitate. Contains about 73 per cent water; the remainder is calcium chloride and less than 1 per cent of a saponifiable resinous material.	Use 1 gallon in the gaging water for one barrel of cement.
25	Turbid liquid. Contains about 60 per cent water; the remainder is calcium chloride.	Use 1 quart in the gaging water per bag of cement.
26	Clear solution. Contains about 73 per cent water; the remainder is calcium chloride.	Do.
27	Clear solution. Contains about 65 per cent water; the remainder is calcium chloride.	Add 1 gallon to each 12 gallons of water and use as gaging water.
28	Light yellow colored turbid solution. Contains about 70 per cent water; the remainder is essentially calcium chloride.	Use 1 gallon in the gaging water per barrel of cement.
30	Turbid solution. Contains about 60 per cent water; the remainder is calcium chloride and a small amount of calcium hydroxide.	Use 1 gallon to each 10 gallons of water and use as gaging water.
33	Dark purple colored liquid. Contains about 60 per cent water colored with a purple dye; the remainder is calcium chloride.	Use 1 quart in the gaging water per bag of cement.
35	Turbid solution. Contains about 73 per cent water; the remainder is calcium chloride.	Do.
7	Calcium oxychloride powder	Use 5 pounds to a bag of cement and mix with the cement before adding water.

Group No. 2. CALCIUM CHLORIDE PLUS MISCELLANEOUS MATERIALS

21	Thick white semiliquid. Contains about 75 per cent water; the remainder is calcium chloride, silica, and calcium stearate. About 13 per cent of fatty acids are present as stearate.	Mix 1 gallon of material to 1 gallon of water. Use 2 quarts of the mixture as gaging water per bag of cement.
31	White paste. Contains about 73 per cent water; the remainder is calcium chloride and calcium stearate. About 4 per cent of fatty acids are present as stearate.	Use two-thirds quart in gaging water per bag of cement.
34	Gray turbid liquid. Contains about 57 per cent water; the remainder is calcium chloride, aluminum chloride, and silica.	Use 1 quart in gaging water for 100 pounds of cement.
37	Thick white liquid. Contains about 65 per cent water; the remainder is calcium chloride and ammonium stearate. About 11 per cent of fatty acids are present as stearate.	Use 1 gallon to each 33 gallons of gaging water.
38	Black colored, odorless liquid. Contains about 66 per cent water; the remainder is calcium chloride, aluminum chloride, silica, and a black dye.	Use 1 quart to one bag of cement; add to the mix after the water has been added.
39	Yellow colored paste. Contains about 84 per cent water; remainder is calcium chloride and colloidal silica.	Use 1 part of paste to 10 parts of water as gaging water.

Group No. 3. SOAPS

13	Thick white paste. Contains about 89 per cent of water; the remainder is ammonium stearate. About 11 per cent of fatty acids are present as stearate.	Use 1 gallon to 34 gallons of water and use as gaging water.
14	Thick white paste. Contains about 87 per cent of water; the remainder is ammonium stearate. About 13 per cent of fatty acids are present as stearate.	Use 1 gallon to 32 gallons of water and use as gaging water.
18	Thick white semiliquid completely soluble in water. Contains sodium stearate. About 9 per cent of fatty acids are present as stearate.	Use 6 pounds in gaging water per barrel of cement.
22	Thick white paste. Contains water and ammonium stearate. About 23 per cent of fatty acids are present as stearate.	Use 2 pounds in gaging water per bag of cement.
23	Thick white paste. Contains water and ammonium stearate. About 19 per cent of fatty acids are present as stearate.	Do.
29	Yellow turbid liquid. Contains water, ammonium oleate, and a very small amount of calcium chloride. About 5 per cent of fatty acids are present as oleate.	Use 1 quart in gaging water per bag of cement.
36	Thick cream colored liquid. Contains about 85 per cent water; remainder is ammonium oleate and a small amount of unsaponifiable oil.	Use 1 gallon to each 36 gallons of water as gaging water.

TABLE 1.—*Composition and method of incorporation of integral waterproofing materials*—Continued

Group No. 4. HYDRATED LIME PLUS SOAP

Material No.	Composition	Method of incorporation
1	White powder. Contains dolomitic hydrated lime and calcium stearate. About 5 per cent of fatty acids are present as stearate.	Use 2 pounds to one bag of cement. Mix dry with cement.
2	White powder. Contains dolomitic hydrated lime and calcium stearate. About 10 per cent of fatty acids are present as stearate.	Use 2 per cent by weight of cement and mix with the cement before adding water.
3	White powder. Contains an impure dolomitic hydrated lime and calcium stearate. About 9 per cent of fatty acids are present as stearate.	Use 2 pounds per bag of cement and mix dry with the cement.
5	White powder. Contains hydrated lime, alum, and calcium stearate. About 9 per cent of fatty acids are present as stearate.	Do.
6	White powder. Contains hydrated lime and calcium stearate. About 2 per cent of fatty acids are present as stearate.	Do.
8	Pink powder. Contains hydrated lime, calcium oleate, and small amount of iron oxide. About 12 per cent of fatty acids are present as oleate.	Use 2 per cent of weight of cement and mix dry with the cement.

Group No. 5. FINELY SUBDIVIDED MATERIALS USED AS FILLERS

9	Diatomaceous silica	Use 3 pounds per bag of cement and mix with cement before adding water.
46	High calcium hydrated lime	Use 10 per cent of the weight of cement and mix with cement before adding water.
47	Hydrated dolomitic lime	Do.
48	Finely ground silica and bentonite	Use 5 per cent of the weight of cement and mix with cement before adding water.
49	Finely ground potter's flint	Use 10 per cent of the weight of cement and mix with cement before adding water.
50	Light gray powder; finely ground soapstone	Do.

Group No. 6. MISCELLANEOUS MATERIALS

4	White powder. Contains barium sulphate, calcium and magnesium silicate, and about 7 per cent of uncombined low melting fatty acids.	Use 2 pounds to 100 pounds of cement and mix with the cement before adding water.
10	Gray powder. Contains finely ground silica and from 1 to 2 per cent of naphthalene.	Use 6 pounds to 135 pounds and 14 ounces of cement and mix with the cement before adding water.
11	Thick white paste. Contains about 85 per cent water; the remainder is colloidal silica and a fluosilicate.	Use 2¼ pounds to one bag of cement and thoroughly mix with the gaging water.
12	Thick yellow paste. Contains about 40 per cent of water, about 30 per cent of petroleum jelly, and about 30 per cent of lime.	Use 1 pound for each bag of cement and add to the gaging water.
15	Thick gray colored paste. Contains cellulose material and wax held in an ammonical copper solution.	Use in the proportion of 1 part to 20 parts of gaging water.
16	Thick gray colored paste. Composition is only slightly different than No. 15.	Do.
17	Thick dark green paste. Similar to No. 15 and No. 16, but does not contain as much wax and cellulose as the other two.	Use in the proportion of 1 part to 28 parts of gaging water.
19	Thick white paste. Contains about 37 per cent water; the remainder is barium sulphate, silica, calcium, and about 6 per cent of uncombined low melting fatty acid.	Use 2 pounds per bag of cement and add to the gaging water.
32	Thick brown colored liquid with an aromatic odor. Contains about 85 per cent water; the remainder is silica, hydrated lime, and alum.	Use 1 gallon to one barrel of cement and add to the gaging water.
40	Thick black liquid. Contains coal tar cut with benzene	Use 1 pound to each 100 pounds of cement. Add to the mix after the water has been added.

TABLE 1.—*Composition and method of incorporation of integral waterproofing materials*—Continued

Group No. 6. MISCELLANEOUS MATERIALS—Continued

Material No.	Composition	Method of incorporation
41	Portland cement containing a water repellent material, such as calcium stearate.	Use in the place of and in the same proportion as the standard cement.
42	Portland cement containing a specially prepared form of calcium sulphate.	Do.
43	Butyl stearate	Use 1 pound to each 100 pounds of cement. Add to the mix after the water has been added.
44	Heavy oil. Contains mineral oil and about 12 per cent of stearic acid.	Use 2 quarts tol 1 bag of cement. Add to the mix after the water has been added.
45	Thick brown-colored liquid. Contains sodium silicate and an organic nitrogenous material resembling glue.	Use 1.2 kg of solution to 100 kg of cement and add to the mixing water.

V. DISCUSSION OF RESULTS

1. PLAIN CONCRETE

The average results obtained in six different batches of concrete of three specimens each are presented in Figure 1. These batches were made of 1 : 3 : 6 concrete, free from waterproofing admixtures. The deviation of the results of each batch from the average of the entire group, represented by the dash line, indicates the probable error in the results reported for mixes containing waterproofing materials. The average of this group of specimens is used as a basis for comparing the relative efficiencies of the compounds tested.

The plain concrete specimens were not noticeably affected by wire brushing. The very slight increase in permeability after this treatment is negligible.

The permeability of all the specimens was increased by drying. The initial permeability was high but decreased appreciably in one month's time.

The results graphically presented in Figure 2 show the deviations from the average which occurred after one year, after wire brushing and after one month's drying of the specimens in the air of the laboratory.

The results obtained with the individual specimens of plain concrete and also with the concrete containing waterproofing compounds were quite consistent except after the specimens were dried for one month in the air of the laboratory. These results, in some cases, were quite erratic.

2. CALCIUM CHLORIDE GROUP (FIGS. 2 AND 3)

Permeability.—Nos. 24, 25, 26, 27, 28, 30, 33, and 35 are essentially calcium chloride in a water solution, containing from 30 to 40 per cent of the solute. They were added to the concrete mix in the proportion of 1 quart of the solution to one bag of cement except Nos. 27 and 30. About 3 quarts of No. 27 and about 4 quarts of No. 30 were added per bag of cement. No. 7 is a calcium oxy-

chloride powder. Five pounds of this sample were added per bag of cement to the dry mix.

The mixes containing Nos. 27 and 30 were markedly less permeable than the standard for the earlier periods. In these two the calcium chloride was present in greater quantities than in the others, as indicated above. No. 7, the calcium oxychloride, also gave a less permeable mix.

At the 28-day period Nos. 7 and 30 gave the same results as the standard, while the other samples showed a greater permeability. At

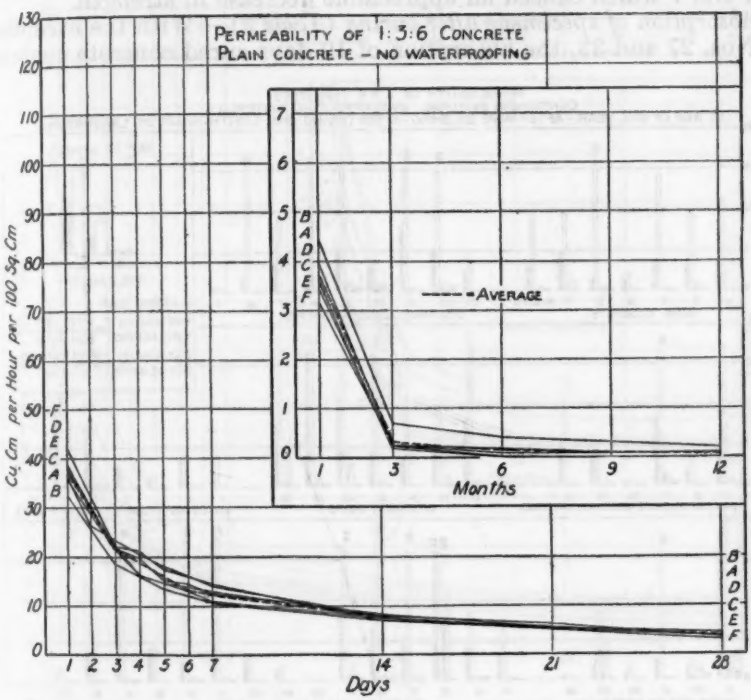
PERMEABILITY OF 1:3:6 CONCRETE
PLAIN CONCRETE – NO WATERPROOFING
Cu. Cm per Hour per 100 Sq. Cm
Days
Months
AVERAGE
F D E C A B
B A D C E F

FIGURE 1.—*Permeability of 1:3:6 concrete containing no waterproofing*

the end of one year Nos. 7 and 24 were impermeable. Nos. 25 and 28 were more permeable than the standard. The other samples of this group were about the same as the standard.

Wire brushing had no appreciable effect on the permeability of any of the specimens of this group.

One month's drying in the laboratory caused an appreciable increase in the initial permeability of Nos. 25 and 26. The amount of water passing through these specimens decreased considerably, but they remained more permeable than the standard at the end of one month. No. 28 showed a slight increase in permeability, after drying, both initially and at the end of the test. Nos. 24, 27, 30, 33, and 35 did not vary appreciably from the standard. No. 7 did not show an increase in permeability after drying and was the least permeable in this group.

Compressive strength (*Table 2*).—The addition of this group of samples to the concrete caused an increase in strength in all the specimens at seven days, compared to the untreated concrete.

The 28-day strength was higher than the standard in specimens containing Nos. 24, 25, 26, 30, and 35, while Nos. 27, 28, and 33 did not show a noticeable deviation from the standard. No. 7 showed a slight decrease in strength. As compared to the standard the 1-year strength was higher for the treated concrete, with the exception of Nos. 28 and 33 which remained about the same as the standard, and No. 7 which caused an appreciable decrease in strength.

Absorption of specimens after curing (*Table 2*).—With the exception of Nos. 27 and 33, the absorption of 19 days cured concrete contain-

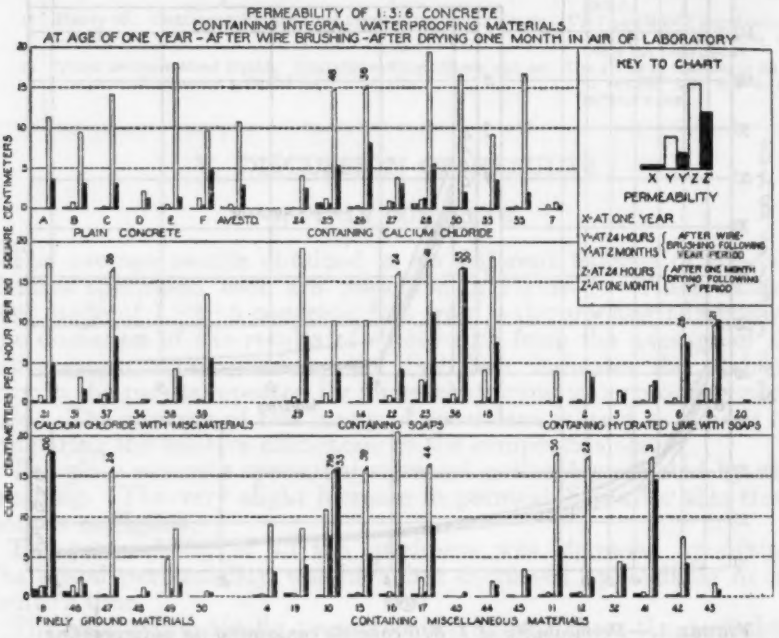
PERMEABILITY OF 1:3:6 CONCRETE
CONTAINING INTEGRAL WATERPROOFING MATERIALS
AT AGE OF ONE YEAR - AFTER WIRE BRUSHING - AFTER DRYING ONE MONTH IN AIR OF LABORATORY
CUBIC CENTIMETERS PER HOUR PER 100 SQUARE CENTIMETERS
KEY TO CHART
X Y Y Z Z'
PERMEABILITY
X-AT ONE YEAR
Y-AT 24 HOURS (AFTER WIRE-BRUSHING FOLLOWING YEAR PERIOD)
Y-AT 2 MONTHS
Z-AT 24 HOURS (AFTER ONE MONTH DRYING FOLLOWING Y PERIOD)
Z-AT ONE MONTH
A B C D E F AVE.STD.
PLAIN CONCRETE
CONTAINING CALCIUM CHLORIDE
CALCIUM CHLORIDE WITH MISC. MATERIALS
CONTAINING SOAPS
CONTAINING HYDRATED LIME WITH SOAPS
FINELY GROUND MATERIALS
CONTAINING MISCELLANEOUS MATERIALS

FIGURE 2.—*Permeability of 1:3:6 concrete containing integral waterproofing materials at the age of one year, after wire brushing and after drying one month in the air of the laboratory*

ing this group of waterproofings was lower than that of untreated concrete, for 1, 2, and 4 hours immersion in water. The absorption for 24 and 48 hours immersion was about the same for both treated and untreated concrete.

After curing for one year the specimens containing this group did not vary appreciably from the untreated concrete when subjected to 1, 2, and 4 hours' immersion in water. The concrete containing No. 24 was the only exception, showing a higher absorption than the standard for all periods of immersion. The absorption of the treated specimens for the 24 and 48 hour periods was less than for the untreated concrete, except for Nos. 24 and 33.

3. GROUP CONTAINING CALCIUM CHLORIDE PLUS MISCELLANEOUS MATERIALS (FIGS. 2 AND 4)

Permeability.—Waterproofings Nos. 21, 31, 34, 37, 38, and 39 contain calcium chloride with the addition of other materials, such as soap, silica, and aluminum chloride. The quantity of each compound incorporated into the mix per bag of cement was 1 quart of No. 21, ⅞ quart of No. 31, nearly 1 quart of No. 34, 1.1 quarts of No. 37, 1 quart of No. 38, and about 4 quarts of No. 39.

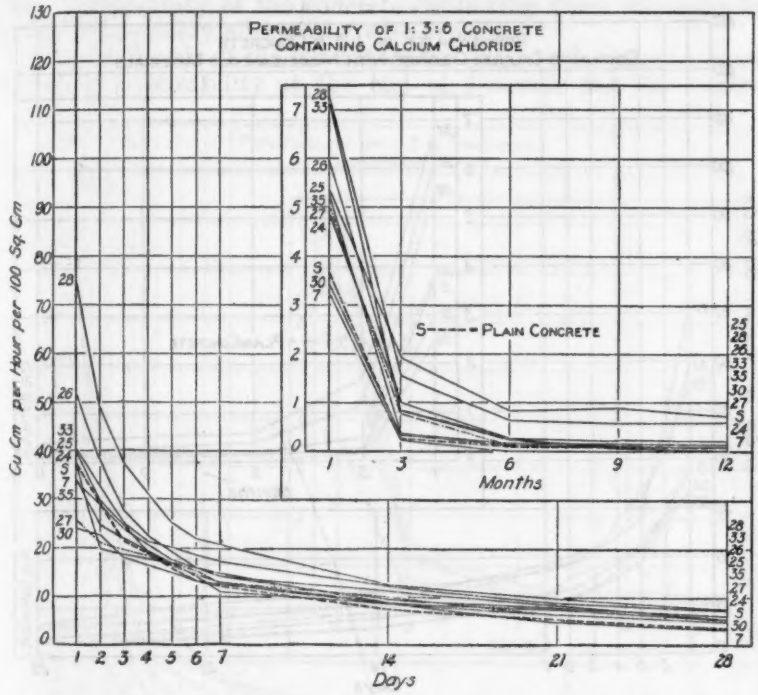

FIGURE 3.—*Permeability of 1:3:6 concrete containing calcium chloride*

The initial permeability of concrete containing Nos. 21, 37, and 39 was greater than that of the untreated concrete. At 14 days the permeability of No. 39 decreased and became the same as that of the standard at 28 days, remaining in this relative position for the other periods, while Nos. 21 and 37 remained appreciably more permeable throughout the test.

Nos. 31, 34, and 38 caused a negligible difference in permeability initially and at seven days as compared to the untreated concrete. From the 7-day period to the end of the test Nos. 31 and 34 caused a decrease in permeability, while No. 38 showed an increase, but approached the standard at nine months.

The permeability of this group was not altered appreciably by wire brushing.

A month's drying of these specimens in the air of the laboratory increased the permeability of the concrete containing No. 37, while Nos. 21 and 39 yielded nearly the same results as the standard.

Concrete containing No. 34 was the least affected by the drying treatment being less permeable than the standard. Nos. 31 and 38 also caused a decrease in permeability.

Compressive strength (*Table 2*).—With the exception of No. 31, the addition of the waterproofings only slightly affected the strength at any age.

Absorption after curing (*Table 2*).—This group caused a decrease in absorption for the 1, 2, and 4 hour periods, Nos. 21 and 37 causing a marked decrease. Nos. 21 and 37 were less absorptive at 24 and 48

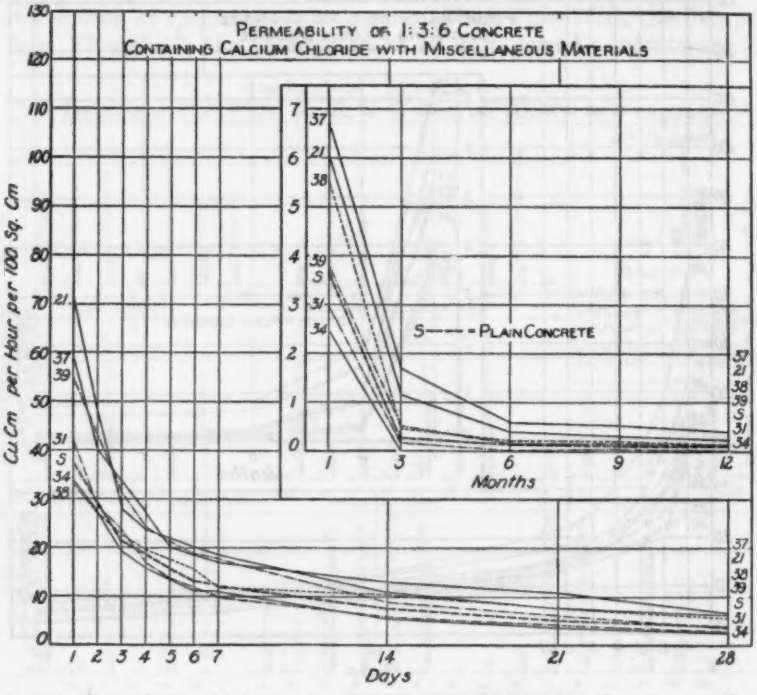
PERMEABILITY OF 1:3:6 CONCRETE
CONTAINING CALCIUM CHLORIDE WITH MISCELLANEOUS MATERIALS
Cu Cm per Hour per 100 Sq. Cm
Days
Months
S---- = PLAIN CONCRETE

FIGURE 4.—*Permeability of 1:3:6 concrete containing calcium chloride plus miscellaneous materials*

hours. The other specimens did not vary appreciably from the standard.

When cured for one year, Nos. 21, 31, 34, and 39 caused a decrease in absorption for all periods. The decrease for these specimens was more marked in the later periods.

4. GROUP CONTAINING SOAP (FIGS. 2 AND 5)

Permeability.—Nos. 13, 14, 18, 22, 23, 28, and 36 are either pastes or liquids containing soaps of different compositions. The amount of each compound incorporated into the mix per bag of cement was approximately 2.2 pounds of No. 13, 2.4 pounds of No. 14, 1.5 pounds of No. 18, 2 pounds of No. 22, 2 pounds of No. 23, 2 pounds of No. 29, and 2.1 pounds of No. 36.

In all cases the concrete mixes containing these materials were more permeable than the standard except a decrease in permeability for

the last period was shown by those containing less soap. Nos. 22 and 23 containing a high percentage of a stearate soap and No. 36 containing a relatively high percentage of an oleate soap did not show as great a decrease in permeability for the last period as was caused by the compounds containing smaller quantities of soaps. A marked decrease resulted with the use of Nos. 29 and 36 in permeability at three months and showing, but a small further decrease in the later periods. No. 36 containing more soap than No. 29 caused a greater permeability.

The permeability of the concrete containing these waterproofings was not appreciably affected by wire brushing.

Drying in the air of the laboratory for one month caused a marked increase in permeability at the end of 1-month test for concretes

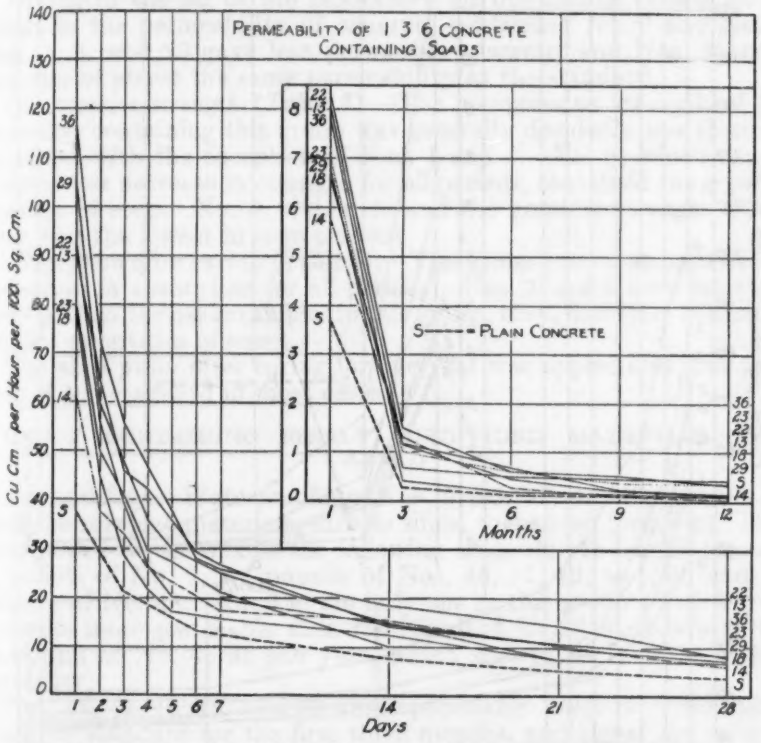

FIGURE 5.—*Permeability of 1:3:6 concrete containing soaps*

containing Nos. 29, 23, 36, and 18. Nos. 13, 14, and 22 gave results about the same as standard.

Compressive strength (*Table 2*).—This group showed a compressive strength at seven days slightly lower than that of the standard, except Nos. 13 and 22 which were the same as standard.

The 28-day strength was higher for No. 13; No. 14 was about the same as standard. The other samples caused a decrease in strength.

The 1-year strength of concrete containing waterproofings Nos. 13, 22, and 23 was about the same as standard. The other samples, however, gave strengths lower than the untreated concrete.

Absorption after curing (*Table 2*).—The absorption of concrete containing these soaps was less than that of the standard for the first three periods, except in one instance. In the last two periods, No. 36 showed less absorption; the other samples were about the same as standard.

After curing for one year, Nos. 13, 29, and 36 caused a reduction in absorption for all periods, the reduction being quite appreciable

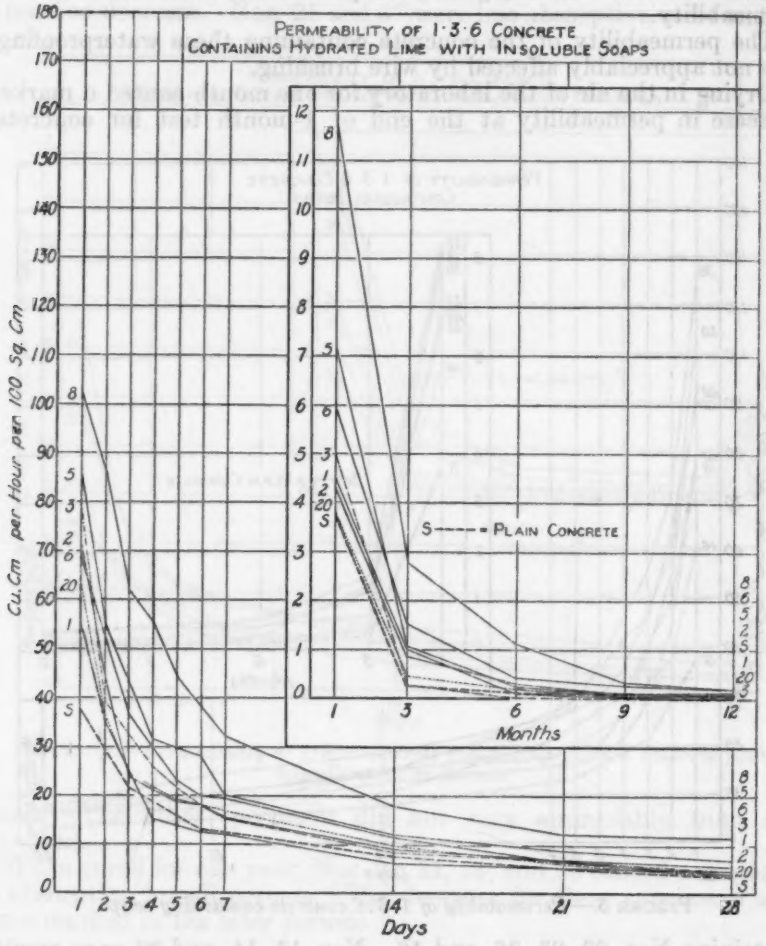

FIGURE 6.—*Permeability of 1:3:6 concrete containing hydrated lime with insoluble soaps*

in the last two periods. The other samples showed only a slight deviation from the standard.

5. GROUP CONTAINING HYDRATED LIME AND SOAP (FIGS. 2 AND 6)

Permeability.—Waterproofings Nos. 1, 2, 3, 5, 6, and 8 are powders containing hydrated lime and varying quantities of insoluble soaps. No. 20 is a paste consisting of lime, alum, and an insoluble soap.

The samples were incorporated into the mix in the following proportions per bag of cement: 2 pounds of Nos. 1, 3, 5, and 6, 1.9 pounds of Nos. 2 and 8, and 1.5 quarts or approximately 3 pounds of No. 20.

This group yielded concrete that gave a high initial permeability. This decreased rapidly for the first few days although No. 8 remained high in permeability for the entire test. The group in general shows a greater permeability than standard throughout the test, approaching the standard, however, at the end of the year. Concrete containing sample No. 1 is the only one that shows a permeability less than the standard and after 21 days it is about the same as standard for the remainder of the test.

The permeability of concrete containing these waterproofings was not affected by wire brushing.

Drying in the air of the laboratory for one month caused an increase in the permeability of concrete containing No. 6 and No. 8. Nos. 1, 3, and 20 gave less permeable concrete, and Nos. 2 and 5 concrete of about the same permeability as the standard.

Compressive strength (*Table 2*).—The compressive strength of the concretes containing this group was generally decidedly less than the standard with the exception of Nos. 1 and 6. No. 8, which caused the greatest decrease in strength for all periods, contained the greatest amount of soap. No. 6, which showed the greatest strength at one year, was the lowest in soap content.

Absorption after curing (*Table 1*).—This group caused an appreciable reduction in absorption for all periods. Nos. 1 and 6 were more absorbent than the other samples in this group; they, however, contained smaller quantities of soap.

The absorption after curing for one year was appreciably less than that of the standard in most cases.

6. GROUP CONTAINING FINELY SUBDIVIDED MATERIALS (FIGS. 2 AND 7)

Permeability.—Waterproofings Nos. 9, 46, 47, 48, 49, and 50 are finely subdivided materials, such as silica, soapstone, lime, etc. They were added to the mix in the following amounts per bag of cement: 3 pounds of No. 9, 9.4 pounds of Nos. 46, 47, 49, and 50, and 4.7 pounds of No. 48. No. 9 is the only one in this group which gave a concrete more permeable than the standard for all periods with the exception of No. 46 at one year, which showed an increase in permeability.

Nos. 46, 47, 48, 49, and 50 were appreciably lower in permeability than the standard for the first three months, and about the same as standard for the remainder of the test. The behavior of No. 46 for the last three months was abnormal.

Wire brushing caused an increase in the permeability of No. 49. The others were not appreciably affected.

One month's drying in the air of the laboratory caused an abnormal increase in the permeability of No. 9. No. 47 was more permeable than the standard 24 hours after drying, but was approximately the same as standard at the end of a month. Nos. 46, 48, 49, and 50 were less permeable than the standard.

Compressive strength (*Table 2*).—The incorporation of these waterproofings in the mix gave, in general, a concrete with a strength equal to or greater than the standard.

Absorption after curing (*Table 2*).—The absorption of concrete containing the materials in this group was practically the same as standard. After curing one year the absorption was considerably greater than that of the standard, with the exception of No. 9.

7. GROUP CONTAINING MISCELLANEOUS MATERIALS (FIGS. 2, 8, AND 9)

Permeability.—Waterproofings Nos. 4, 10, 15, 16, 17, 19, 40, 44, 45, 11, 12, 32, and 43 are of various compositions. Nos. 42 and 41 are special cements, the latter containing calcium stearate. The amounts incorporated in the mix per bag of cement were approximately 1.9 pound of Nos. 4 and 19, 4.2 pounds of No. 10, 3.8 pounds of Nos. 15 and 16, 2.7 pounds of No. 17, 0.94 pounds of Nos. 40 and 43, 4 pounds

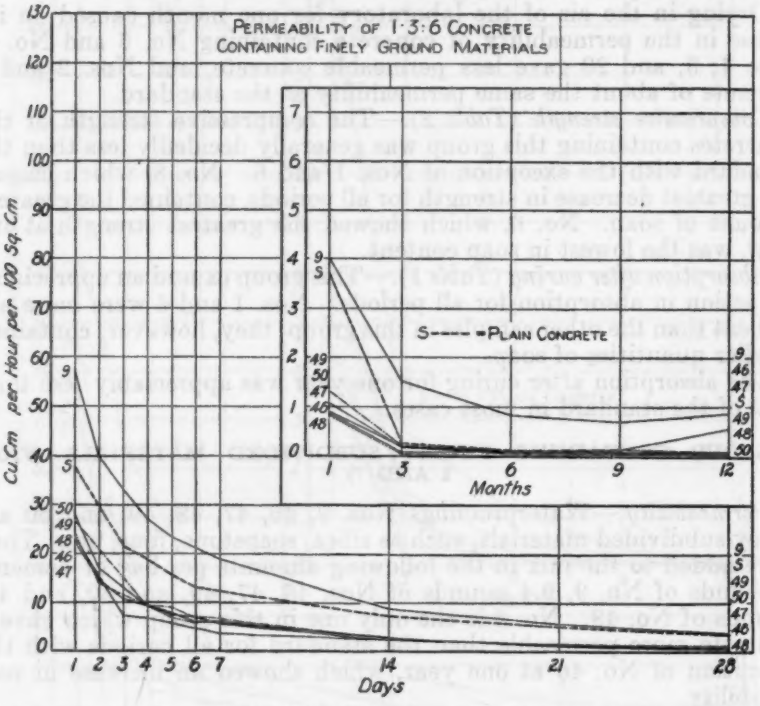

FIGURE 7.—*Permeability of 1:3:6 concrete containing finely ground materials*

of No. 44, 1.2 pounds of No. 45, 2¼ pounds of No. 11, 1 pound of No. 12 and 2 pounds of No. 32. Nos. 41 and 42 were used in place of the regular cement.

Nos. 4, 10, and 19 yielded concrete that was highly permeable at the start of the test, and remained so to the end of the test. No. 44 showed a marked decrease in permeability. No. 40 showed a higher initial permeability than the standard. This decreased equaling the standard at 14 days and was even less permeable for the remainder of the test. Nos. 15, 16, and 17 were of the same approximate composition. The specimens containing these three and No. 41 were more permeable than the standard at all periods. Nos. 42 and 45 yielded concretes that were less permeable for the first three months,

and about the same as standard from three months to the end of the year. The concrete containing No. 11 was more permeable than the standard for the first three months and about the same as standard from that period until the end of the test. No. 12 yielded a concrete of about the same permeability as the standard; however, in the later periods the permeability increased slightly instead of normally decreasing in permeability. Concrete containing No. 43 was about

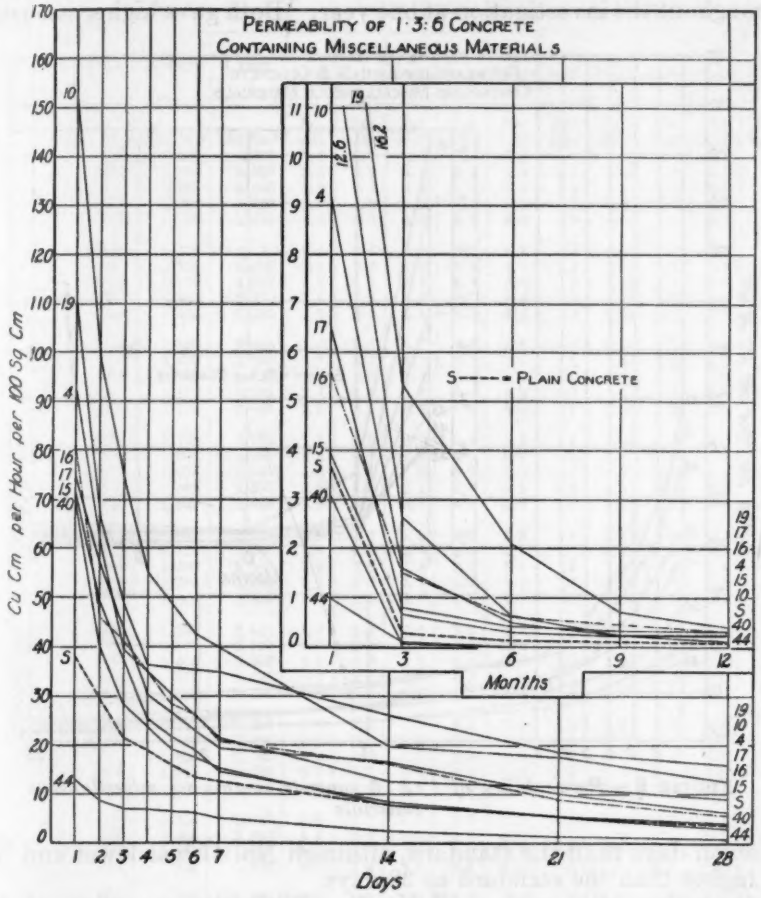

FIGURE 8.—*Permeability of 1 : 3 : 6 concrete containing miscellaneous materials*

the same as standard. Concrete containing No. 32 was less permeable than the standard.

The concretes containing the samples of this group were not affected by wire brushing with the exception of No. 10.

One month drying in the air of the laboratory caused a decided softening of the concrete containing No. 10. The permeability of Nos. 4, 19, 45, 12, 32, and 42 were about the same as the standard. Nos. 15, 16, 17, 11, and 41 were more permeable than standard and Nos. 40, 43 and 44 were less permeable.

Compressive strength (*Table 2*).—The compressive strength of concrete containing the waterproofings in this group were generally lower than that of the standard. No. 10 showed a marked reduction in strength, yielding the lowest strength of all materials tested. No. 45 also showed an appreciable reduction in strength. Nos. 11 and 15 show strengths about the same as standard; Nos. 12 and 32 show a higher strength than standard at one year. Nos. 41 and 42, which were special cements, gave lower strength than the cement used throughout the investigation at one year. Both gave higher strengths

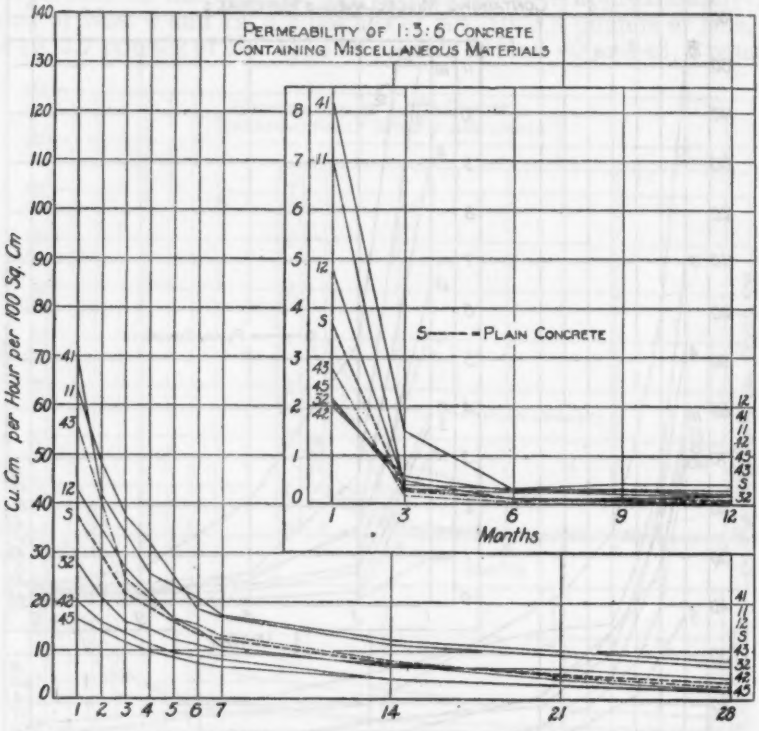

FIGURE 9.—*Permeability of 1 : 3 : 6 concrete containing miscellaneous materials*

at seven days than the standard, although No. 41 was lower and No. 42 higher than the standard at 28 days.

Absorption after curing (*Table 2*).—With the exception of the concretes containing Nos. 40, 45, and 12 which showed about the same absorption as standard and Nos. 11 and 32 which were more absorbent than standard, the other waterproofings of this group caused a reduction in absorption of varying amounts. No. 43 gave the lowest absorption of all the waterproofings included in this investigation. After curing for one year the concrete containing Nos. 4, 10, 17, 44, 41, and 43 showed a lower absorption than standard. Nos. 44 and 43 showed a marked reduction in absorption. Nos. 11 and 19 showed an increase in absorption. Nos. 12, 15, 16, and 45 caused a higher absorption for the first three periods and lower absorption for the last two periods. Nos. 32 and 42 were about the

same as standard for the first two periods but less absorbent for the last three periods. No 40 was slightly lower for the early periods and slightly higher at 24 and 48 hours.

TABLE 2.—*1:3:6 concrete containing integral waterproofing materials*

No.	Compressive strength, 3 by 6 inch cylinders			Absorption, 3 by 6 inch cylinders									
				Cured 19 days					Cured 1 year				
	7 days	28 days	1 year	1 hour	2 hours	4 hours	24 hours	48 hours	1 hour	2 hours	4 hours	24 hours	48 hours
	Lbs /in.²	*Lbs./in.²*	*Lbs /in.²*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
Standard	840	1,780	2,900	2.7	3.7	4.8	5.3	5.4	0.9	1.1	1.5	3.1	3.9
24	970	1,910	3,090	2.0	3.1	4.2	5.3	5.4	1.1	1.5	1.9	4.0	4.5
25	1,100	1,855	3,145	2.2	3.2	4.4	5.4	5.6	.8	1.1	1.4	2.9	3.8
26	1,085	2,075	3,220	1.9	3.0	3.9	5.2	5.3	.8	1.0	1.2	2.4	3.3
27	1,070	1,730	3,190	3.2	3.9	5.0	5.3	5.5	.8	1.0	1.2	2.3	2.8
28	1,040	1,775	2,845	2.4	3.4	4.5	5.3	5.3	.8	1.1	1.4	2.8	3.7
30	1,085	1,840	3,125	2.1	3.6	4.1	5.3	5.4	.9	1.1	1.3	2.3	2.8
33	970	1,750	2,820	3.4	4.4	5.1	5.4	5.4	.8	1.1	1.4	2.9	3.9
35	965	1,940	2,970	1.9	2.8	3.9	5.2	5.4	.8	1.0	1.2	2.4	2.9
7	925	1,555	2,635	2.2	3.1	4.1	5.4	5.5	.8	1.0	1.3	2.8	3.6
21	850	1,830	2,540	1.5	2.1	2.7	4.6	4.8	.8	1.0	1.2	2.4	3.1
31	765	1,470	2,240	2.1	3.2	4.3	5.3	5.4	.6	.9	1.2	2.3	3.0
37	900	1,880	2,770	1.7	2.3	3.1	4.8	5.1	.9	1.2	1.5	3.0	3.6
34	1,125	1,870	3,165	2.4	3.4	4.5	5.3	5.3	.7	.8	1.2	2.5	3.2
38	1,045	1,775	3,005	2.3	3.2	4.3	5.5	5.6	.9	1.2	1.5	2.9	3.7
39	955	1,780	2,765	1.8	2.8	3.9	5.4	5.5	.8	.9	1.2	2.7	3.8
29	715	1,365	2,000	2.8	3.5	4.4	5.0	5.2	.6	.8	.9	2.0	2.8
13	875	2,015	3,045	1.8	2.4	3.0	5.0	5.2	.7	.9	1.2	2.1	2.5
14	775	1,845	2,380	1.8	2.4	3.1	4.9	5.1	1.0	1.3	1.7	3.3	3.8
22	830	1,605	2,890	1.9	2.4	3.2	4.9	5.2	1.0	1.3	1.6	3.0	3.6
23	710	1,695	2,745	1.9	2.6	3.5	5.3	5.5	.9	1.2	1.5	3.2	3.8
36	555	1,420	2,045	1.3	2.0	2.4	3.8	4.1	.7	1.0	1.2	2.1	2.6
18	695	1,380	2,040	1.9	2.7	3.5	4.8	5.0	.8	1.0	1.3	2.5	3.1
1	810	1,705	2,775	2.3	3.0	3.8	5.2	5.3	.8	1.0	1.6	3.3	3.8
2	790	1,535	2,320	1.7	2.3	3.0	4.5	4.7	.6	.8	1.0	2.2	3.0
3	930	1,530	2,410	1.7	2.2	2.8	3.9	4.7	.6	.8	1.0	2.1	2.7
5	765	1,365	2,100	1.7	2.1	2.6	4.0	4.2	.7	.8	1.0	2.0	2.4
6	880	1,505	2,910	2.1	3.0	4.0	5.0	5.1	.8	1.0	1.3	2.8	3.4
8	530	875	1,525	1.7	2.1	2.7	4.3	4.7	.7	.9	1.0	2.0	2.6
20	735	1,320	2,105	1.6	2.1	2.7	4.3	4.6	.9	1.1	1.4	2.7	3.4
9	905	1,860	3,330	2.5	3.5	4.3	5.3	5.4	.9	1.2	1.6	3.2	4.1
46	1,170	1,840	3,300	2.5	3.4	4.2	5.1	5.4	1.5	2.0	2.4	3.6	4.0
47	1,080	1,965	3,535	2.4	3.3	4.1	5.0	5.0	1.3	1.7	2.3	3.8	4.1
48	970	1,825	3,020	2.7	3.7	4.8	5.4	5.4	1.5	2.0	2.5	4.2	4.6
49	830	1,800	2,970	2.7	3.7	4.7	5.2	5.2	1.4	1.8	2.4	4.4	4.6
50	790	1,655	2,940	2.8	3.7	4.8	5.3	5.3	1.5	1.8	2.3	4.0	4.5
4	810	1,565	2,390	1.9	2.5	3.1	4.4	4.7	.7	.9	1.1	2.3	2.9
19	610	1,100	1,790	1.7	2.5	3.4	5.0	5.1	1.0	1.3	1.7	3.5	4.2
10	240	455	870	1.7	2.0	2.5	3.8	4.0	.8	1.0	1.1	1.9	2.3
15	845	1,705	2,990	1.0	1.9	2.5	3.6	4.0	1.0	1.3	1.6	2.7	3.1
16	735	1,700	2,750	1.7	2.2	2.7	4.0	4.5	1.2	1.3	1.7	3.1	3.6
17	780	1,725	2,750	1.5	2.0	2.5	3.9	4.3	.8	1.0	1.2	2.1	2.4
40	785	1,470	2,290	2.4	3.5	4.8	5.4	5.6	.8	1.0	1.4	3.4	4.2
44	645	1,480	2,535	1.4	1.9	2.2	3.8	4.5	.5	.7	.8	1.4	1.7
45	515	970	1,640	3.2	3.8	4.3	5.0	5.2	1.2	1.6	1.9	2.6	3.9
11	720	1,775	2,885	3.1	4.1	5.0	5.3	5.4	1.0	1.5	1.8	3.3	3.8
12	775	1,700	3,050	2.9	3.7	4.9	5.2	5.3	1.1	1.4	1.6	2.6	3.1
32	820	1,805	3,160	3.5	4.6	5.3	5.5	5.5	.9	1.1	1.3	2.7	3.4
41	1,080	1,570	2,195	1.4	1.8	2.4	4.1	4.4	.7	.9	1.1	2.0	2.5
42	1,510	2,130	2,760	1.6	2.3	3.2	4.9	5.1	.9	1.1	1.3	2.4	2.9
43	915	1,520	2,640	.7	.9	1.1	2.2	2.8	.5	.5	.6	1.0	1.2

VI. SUMMARY (INTEGRAL WATERPROOFING)

1. The addition of calcium chloride to the 1:3:6 mix of concrete used in this study did not materially reduce its permeability or absorption. It did, however, seem to increase the compressive strength. An increase in the amount of calcium chloride added per bag of cement seemed to decrease the initial permeability.

2. The incorporation of such materials as soap, silica, and aluminum chloride, with calcium chloride in concrete did not reduce the permeability.

3. The presence of soap in addition to calcium chloride caused a reduction in absorption.

4. The usual increase in strength due to calcium chloride was not obtained when soap was present with the chloride.

5. The addition of soap alone to the concrete caused an increase in permeability. The strength of the concrete containing oleate soap was appreciably reduced. In general, the presence of soaps in concrete caused a reduction in absorption; also a higher initial permeability than the other waterproofings used.

6. Hydrated lime mixed with soap and then incorporated in the concrete gave a higher permeability than the standard. It was not as high as when soaps were added alone. The presence of an appreciable quantity of soap and lime in concrete lowered the strength and reduced the absorption.

7. The finely subdivided compounds used as fillers in general reduced the permeability and in general increased the compressive strength. The absorption was about the same or greater than standard.

8. The permeability of concrete was not reduced by the addition of such miscellaneous materials as cellulose and wax, or by the addition of materials containing uncombined fatty acids, fluosilicate, naphthalene, vaseline, butyl stearate, or coal tar. These compounds in general lowered the compressive strength but reduced the absorption. The presence of a mixture of heavy mineral oil and a saponifiable oil reduced the permeability, absorption, and also the strength.

In the above summary the statements are somewhat general and apply more particularly to the results as obtained for all the materials in any group. Close study shows that the individual waterproofings in a group may vary considerably in their properties.

VII. METHOD OF FABRICATION AND TEST OF SURFACE WATERPROOFING

For this part of the investigation a number of 3 by 6 inch concrete cylinders were made. A 1:2:4 mix by volume of Portland cement (meeting the requirements of the United States Government), Potomac River sand, and a gravel graded between No. 4 and three-eighths inch was used with a water-cement ratio of 1.00 by volume. Weighed portions of cement, sand, and gravel were thoroughly mixed in a galvanized iron pan, the water then added and the mixing continued for two minutes. The concrete was then placed in the molds in three layers, each layer being rodded 25 times with a blunt end tamping rod. The surplus was struck off flush with the top of the mold. After 24 hours the forms were removed and the entire surfaces of the cylinders were wire brushed. They were then placed in the damp closet for

curing. At the age of 7 days the specimens were placed on shelves in the laboratory where the air could freely circulate around all surfaces. They were weighed after 14 days in the air and then weighed every day until they reached constant weight. Three cylinders were coated with each of the surface waterproofing materials and placed on the shelves in the laboratory and allowed to dry to constant weight. They were then totally immersed in water and weighed at 15 minutes, 1 hour, 2 hours, 4 hours, 24 hours, 48 hours, 72 hours, and each succeeding week for one year. The cylinders were then placed on the shelves of the laboratory for one month, again weighed and immersed in water. Weighings were made on the cylinders so treated at 15 minutes, 1 hour, 2 hours, 24 hours, 48 hours, 72 hours, 1 week, and each succeeding week until 2 months old and again at 9 months. Several uncoated cylinders were dried to constant weight, immersed in water and weighed at the same intervals of time as the coated cylinders.

The absorption was computed from the recorded weights, and is reported in per cent of the dry weight. The results obtained on the three cylinders from each mix were averaged and are presented in Table 4.

No specimens were prepared, as in the study of the integral waterproofings, which were tested under a head. It was assumed that if a material allowed water to penetrate into the treated specimen when immersed in water, it would also be permeable under any greater head. The procedure adopted gave a good value for rate of penetration of water through the applied waterproofing mediums. Further, since practically all of the materials sooner or later showed marked permeability, this simple test procedure seems to have been adequate. It does not indicate, however, that the few materials which appear to be satisfactory at the end of a year, might not have shown considerable permeability under some head.

No membranes composed of alternate layers of felt, burlap, etc., and bituminous products, were included in this study. This method of waterproofing although undoubtedly the most costly one, is so universally acknowledged as being satisfactory that it was not deemed necessary to consider it.

This study of coatings was confined to their use between the source of water and the concrete and not to the case where the concrete is between the source and the coating. In other words, the coatings were considered on the same basis as the integral waterproofings, namely, original means of keeping concrete water-tight applied approximately at the time of making the concrete, and not remedial means applied some time in the later life of the concrete when unanticipated leakage has occurred. This special case of waterproofing has not been considered at all.

VIII. SURFACE WATERPROOFING MATERIALS

1. COMMERCIAL NAMES

The materials used in this investigation were furnished by the manufacturer under the following trade names:

Am. Builders' Transparent Waterproofing (A. B.–6).
Am. Builders' Plaster Bond (A. B.–5).
Anti Hydro.
Aquabar Clear Coat No. 2.
Aquabar Elastic Cement Coating No. 6.
Aquabar Mastic Cement.
Aquanox No. 202.
Butyl Stearate.
Butyl Oleate.
Cresolac Transparent Waterproofer.
Dehydratine No. 2.
Dibutyl Phthalate.
General Fireproofing Ironcote (G. F. 14).
General Fireproofing Brush Coating (G. F. 16).
General Fireproofing Bonding Compound (G. F. 400).
General Fireproofing Transparent Waterproofing (G. F. 100).
Hetzel's Fibrous Roof Koting.
Hydrocide Colorless Liquid A.
Hydroseal No. 640.
Ironite.
Isolite.
Konkerit Primer (liquid).
Konkerit (liquid).
Linseed oil (boiled).
Master Builders' Efflorex.
Master Builders' Masterseal No. 1.
Master Builders' Metallic Waterproofing.
Minwax Clear.
Minwax Clear (heavy).
Minwax Colorless (heavy).
Mortex No. 5.
Mortex No. 5A.
Mortex No. 5B.
Mortex No. 10 Fibrated.
Mortex No. 10 Mastic.
Mortex No. 20.
Mulsomastic.
Penetrite Transparent Compound No. 1.
Penetrite Transparent Compound No. 2.
Protex No. 22.
Protex No. 88.
Protone.
R. O. P. Cement Coating.
R. O. P. Damp Resisting Paint.
Silicate of Soda (concrete special).
Transkote.
Tricosal Normal.
Tricosal S III.
Toxloxpore.
Wa-Co Surface Waterproofing.
Whigelt's Xterior Waterproofing.

2. COMPOSITION AND METHOD OF APPLICATION

The surface waterproofings are grouped in accordance with their chemical compositions. The first group represents those containing asphalt emulsions; the second group, bituminous solutions; the third, finely ground iron; the fourth, cement coatings; the fifth, transparent coatings; and the sixth, paint and varnish coatings.

The composition and method of application are given briefly in Table 3.

TABLE 3.—*Composition and method of application of surface waterproofing material*

Group No. 1. ASPHALT EMULSIONS

Material No.	Composition	Method of application
5	First coat a clay asphalt emulsion; second coat a clay asphalt emulsion containing asbestos.	First coat diluted with 25 per cent water; second coat applied with a trowel to a thickness of one-sixteenth inch after first coat was dry.
6	Clay asphalt emulsion containing asbestos	First coat was No. 8 diluted with 25 per cent of water; second coat was No. 6 applied with a trowel 6 hours after No. 8.
7	Clay asphalt emulsion	2 coats brushed on 24 hours apart.
8	do	First coat thinned with 10 per cent water; second coat applied full strength 24 hours later.
9	do	Applied same as No. 8.
10	do	Do.
13	do	First coat thinned with 20 per cent water; second coat applied full strength 24 hours later.
41	Clay asphalt alcohol emulsion	2 coats flowed on 24 hours apart.
42	Clay asphalt alcohol emulsion containing small amount of calcium chloride.	The concrete was saturated with water and a thin coat of No. 42 mixed with water to a creamy consistency was applied. The second coat was neat cement thinned to a creamy consistency with a solution of half each of No. 42 and water; topping coat floated on consisting of 1 part Portland cement and 2 parts of sand wet with a solution of half each of No. 42 and water. When sufficiently set, the surface was troweled and kept under damp cloth for 48 hours.

Group No. 2. BITUMINOUS SOLUTIONS

16	Asphalt cut in petroluem spirits 74 per cent nonvolatile.	2 brush coats 4 days apart.
18	Asphalt cut in petroleum spirits 57 per cent nonvolatile.	2 brush coats 24 hours apart.
21	Asphalt cut in petroleum spirits 67 per cent nonvolatile.	Do.
23	Mixture of asbestos, asphalt, and petroleum spirits containing 45 per cent asbestos, 50 per cent asphalt, and 5 per cent petroleum spirits.	1 coat applied one-eighth to one-fourth inch thick.
29	Asphalt cut in petroleum spirits 75 per cent nonvolatile. Small amount of asbestos.	1 coat brushed on.
31	Asphalt cut in petroleum spirits 60 per cent nonvolatile.	Do.

Group No. 3. FINELY GROUND IRON

17	Finely ground iron and sal ammoniac	Surface treated with solution of magnesium chloride. No. 17 mixed with water to a whitewash consistency and applied to a well-wetted surface. The surface was then gently wetted during the first day as often as the surface became dry. The 4 succeeding coats were a little thicker and were applied the same as the first coat.
27	do	The surface was saturated with water for 24 hours. Brush coat applied consisting of equal parts of No. 27 and Portland cement of the consistency of heavy paint. This was immediately followed by a plastic coat one-eighth inch thick consisting of No. 27, sand and Portland cement in equal parts by weight.
43	do	Surface thoroughly wet with water. Brush coat then applied of No. 43 thinned with water to a thick paste. Dry in air for 24 hours; wet down with water 4 times during that period. Second coat applied in same manner as first coat. Third coat, consisting of 1 part Portland cement, three-fourths part of sand and one-fifth part of No. 43 mixed with water to a consistency a little thinner than plaster, is brushed on the wet surface. Allowed to set in air for 24 hours, being wet down several times during that period. Fourth coat, consisting of 1 part of cement and three-fourths part of sand mixed with water to a slush a little thinner than plaster, applied to wet surface. Dry in open air 24 hours, being wet down several time during that period.

TABLE 3.—*Composition and method of application of surface waterproofing materials*—Continued

Material No.	Composition	Method of application
	Group No. 4. CEMENT COATINGS	
47	Light yellow colored liquid contains about 73 per cent of water; remainder calcium chloride and less than 1 per cent of saponifiable resinous material.	3 coats of the following mix were applied: 1 gallon No. 47, 3 gallons of water and a half bag of Portland cement.
48	Clear amber colored liquid acid in reaction. Contains about 70 per cent water; remainder calcium chloride, aluminum chloride, and small amount of organic matter.	1 coat of the following mix was applied with a trowel: 1 part of cement to 1½ parts of sand mixed with a 1:1 solution of No. 48 and water.
49	Thick brown liquid with an odor of glue. Contains sodium silicate and an organic nitrogenous material resembling glue.	1 coat of the following mix was applied with a trowel: 1 part of cement and 1½ parts of sand mixed with a solution of No. 49 to 30 parts of water.
	Group No. 5. TRANSPARENT COATINGS	
1	Brown colored liquid. Contains glycol, water, ammonia, alcohol, and unsaponifiable oil.	2 coats 48 hours apart.
2	Butyl stearate	3 coats brushed on 24 hours apart.
3	Butyl oleate	Do.
4	Dibutyl phthalate	Do.
11	Boiled linseed oil	2 coats brushed on 24 hours apart; third coat 3 days later.
46	Dark brown oily liquid. Is a mixture of nondrying fatty oils and mineral oil.	1 coat brushed on.
25	Turbid oily liquid. Contains a nondrying oil, paraffin, and mineral oil.	2 coats brushed on 24 hours apart.
37	China wood oil cut in mineral spirits	Do.
12	Lemon-colored turbid oily liquid. Contains mineral oil, a semihard grease similar to vaseline and a small amount of a saponifiable oil.	2 coats brushed on 48 hours apart.
15	Turbid oily solution. Contains saponifiable material cut in mineral oil.	2 coats brushed on 24 hours apart.
24	Clear light-colored oil. Contains mineral wax dissolved in mineral oil and a small amount of nitrobenzene.	3 coats brushed on 24 hours apart.
26	Light yellow colored oil. Contains paraffin wax cut in light mineral oil.	2 coats brushed on 24 hours apart.
28	Thick viscous liquid. Benzol solution of a semihard material, partially saponifiable and mineral oil.	Do.
32	Clear oily solution. Contains mineral wax cut in petroleum spirits.	2 coats brushed on 48 hours apart.
35	Clear solution with a white precipitate. Contains a saponifiable material cut in petroleum spirits.	2 coats brushed on 24 hours apart.
38	Light yellow colored oil. Contains saponifiable material and paraffin dissolved in low boiling mineral spirits.	Do.
39	Light yellow colored oil. Quite similar to No. 38. Contains less paraffin and larger quantity of saponifiable material than No. 38.	Do.
40	Light yellow colored liquid. Contains a small amount of saponifiable material and paraffin cut in mineral oil.	Do.
36	Clear lemon-colored solution. Contains a saponifiable material cut in turpentine and mineral spirits.	Do.
19	White turbid water solution. Contains a saponifiable material and sodium stearate.	3 coats brushed on 24 hours apart.
50	Solution of sodium silicate.	3 coats applied of a 1:4 solution of No. 50 and water, 24 hours between coats.
	Group No. 6. PAINTS AND VARNISHES	
14	Thick gray gelatinous paste. Contains varnish and asbestos.	Material as received applied with a trowel.
20	Dark-colored oily liquid. Contains mineral oil and a saponifiable oil similar to linseed oil.	2 coats brushed on 24 hours apart.
22	White lead oil paint	First coat thinned with turpentine, 1 pint to 1 gallon of paint; second coat used as received 48 hours after first coat.
30	Gray, zinc oxide oil paint	2 coats brushed on 24 hours apart; first coat thinned with 20 per cent turpentine.
33	White barium sulphate paint	1 coat of No. 33 and 2 coats of No. 34 were applied 24 hours apart.
34	White lead and zinc oil paint	
44	This is a varnish. Contains 60 per cent volatile	2 coats brushed on 48 hours apart.
45	White barium sulphate paint	2 coats brushed on 24 hours apart.

X. DISCUSSION OF RESULTS OF ABSORPTION TESTS UP TO ONE YEAR

1. ASPHALT EMULSIONS

All the concrete specimens coated with asphalt emulsions show very little absorption for the first seven days, with the exception of No. 41. This waterproofing is higher in clay content than the other waterproofings of this group. No. 5, the most efficient of this group, contains a high per cent of asbestos and was applied one-sixteenth inch thick. No. 42 is quite similar to No. 41 in chemical composition, but has been mixed with cement for the second coat and with sand and cement for the third coat. This probably accounts for the difference in efficiency between Nos. 41 and 42. No. 41 is less absorbent than No. 42 for the first few hours, but breaks down quite rapidly after the first few periods. No. 6 contains a small amount of asbestos and was applied one-sixteenth inch thick. The other emulsions are applied in two coats and are not as efficient as the coatings containing asbestos. This group produces an appreciable reduction in absorption compared to the plain concrete.

2. BITUMINOUS SOLUTIONS

Nos. 16, 18, 21, 23, 29, and 31 are asphalts cut in petroleum spirits. No. 23 contains a large percentage of asbestos and No. 29 contains a small amount of asbestos. The first three were applied in two coats and the last two were given one coat. No. 23 was applied one-eighth inch thick with a trowel. All of these show very little absorption for the first few days. Nos. 16 and 29 contain the highest percentage of asphalt of this group. No. 16 was quite low in absorption for the entire test. The difference in absorption between these two materials is probably due to the number of coats applied. Nos. 18 and 31 contain about the same amount of asphalt. Two coats of No. 18 resulted in lower absorption than one coat of No. 31. No. 21 contains a smaller amount of asphalt than No. 16 and a larger amount than No. 18 and has a corresponding efficiency. No. 23 was practically impervious to water throughout the test.

3. FINELY GROUND IRON

Nos. 17, 27, and 43 are finely ground iron mixed with sal ammoniac. They are less absorbent than the standard for the first few periods, but break down rapidly after a few days immersion in water. The difference in absorption is mainly due to the manner of application of the material. No. 17 was applied in five coats, No. 27 in two coats containing the material mixed with cement and sand. The coating was about one-eighth inch thick. No. 43 was applied in four coats, the third coat containing sand and cement and the fourth a slush or finish coat of sand and cement.

4. CEMENT COATINGS

Coatings Nos. 47, 48, and 49 are incorporated with a cement mix and then applied to the surface of the concrete. No. 47 is essentially a solution of calcium chloride. It is mixed with cement to a creamy consistency and applied in three coats. It is less absorbent for the

first few hours, but breaks down quite rapidly. No. 48 is an acid solution of calcium chloride and aluminum chloride. No. 49 is a solution containing sodium silicate and glue. These last two materials are added to a mixture of Portland cement and sand to form a thick mortar and applied to the specimens one-fourth inch thick with a trowel. They are less absorbent than the uncoated concrete, particularly so at the early periods. This may possibly be due to the thick coating of mortar, regardless of the waterproofing added to it.

5. TRANSPARENT COATINGS

Sample No. 1 is a solution containing glycol. This is applied in two coats and is quite efficient for the first few periods but fails rapidly. Nos. 2, 3, and 4 are, respectively, butyl stearate, butyl oleate, and dibutyl phthalate. They were applied in three coats. With the exception of the phthalate these materials are quite efficient. No. 11 is boiled linseed oil and shows relatively excellent results. No. 46 contains a nondrying saponifiable oil and mineral oil. It is less absorbent for the first periods, but breaks down after 24 hours immersion in water. No. 25 contains a nondrying saponifiable oil, mineral oil, and paraffin. It is less absorbent for the first few hours, but breaks down after the first day. No. 37 is China wood oil cut in mineral spirits. This material showed the best results of all the transparent waterproofings tested.

Waterproofings Nos. 12, 15, 24, 26, 28, 32, 35, 38, 39, 40, 36, and 19 are, in general, solutions of paraffin, waxes, etc., in mineral spirits or somewhat similar solvents. No. 50 is a solution of sodium silicate. These 13 waterproofings when applied to concrete are less absorbent than the uncoated concrete for the first few hours, but break down rapidly about the first day.

6. PAINTS AND VARNISHES

Samples Nos. 14, 20, and 44 contain varnish. No. 14 is a varnish mixed with asbestos to form a thick paste and was applied about one-sixteenth inch thick with a trowel. This coating was quite efficient, but started to break down after six months. No. 20 is fairly efficient for the first four hours, but breaks down at 24 hours. No. 44 is quite efficient throughout the test. The paint coatings Nos. 22, 30, 33, 34, and 45 are all quite efficient for the first two or three months, but start to break down at the later periods.

X. DISCUSSION OF RESULTS OF ABSORPTION TESTS SUBSEQUENT TO ONE YEAR

The absorption of the plain concrete was appreciably reduced in comparison with its original absorption at the corresponding time intervals of immersion. (See Table 4.) This was true of most of the coatings. They retained their relative position in per cent water absorbed at the different periods in comparison to the uncoated concrete with the following exceptions: The asphalt emulsion No. 41 was much less absorbent than originally. The bituminous solutions Nos. 29 and 31 showed about the same amounts of absorption as the standard. The finely ground iron coatings Nos. 17 and 43 were less absorbent than originally, but were more absorbent than the standard.

The three cement coatings, Nos. 47, 48, and 49, were appreciably less absorbent than the standard and much less absorbent compared to the corresponding periods of the original absorption results. The transparent coatings Nos. 46 and 25 were much less absorbent than they were originally. These two coatings contained a nondrying saponifiable oil. The paint coatings Nos. 30, 33, 34, and 45 were more absorbent than the standard after the first few hours and also more absorbent than originally at the early periods.

TABLE 4.—*Per cent absorption 3 by 6 inch concrete cylinders coated with surface waterproofing materials*

Time	Asphalt emulsions														
	Material No.														
	Std.	Std.[1]	5	[1]5	6	[1]6	7	[1]7	8	[1]8	9	[1]9	10	[1]10	13
¼ hour	1.7	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1 hour	2.9	.2	0	0	0	0	0	0	0	0	0	0	0	0	0
2 hours	3.5	.2	0	0	0	0	0	0	0	0	0	0	0	0	0
4 hours	4.0	.3	0	0	0	0	.1	0	0	0	0	0	0	0	.1
24 hours	4.4	.9	0	.1	.1	.1	.5	.1	.5	.1	.5	.1	.5	.1	.6
48 hours	4.4	1.1	.3	.1	.4	.1	.8	.1	.8	.1	.8	.1	.8	.1	.9
72 hours	4.7	1.3	.3	.1	.5	.1	1.0	.1	1.0	.1	1.1	.1	1.1	.1	1.1
7 days	4.7	1.7	.6	.1	.8	.1	1.9	.2	1.8	.2	2.0	.3	2.0	.2	1.8
14 days	4.7	2.0	.8	.1	1.1	.1	2.5	.3	2.4	.3	2.8	.3	2.7	.3	2.4
21 days	4.8	2.2	.9	.2	1.3	.2	2.8	.4	2.8	.4	3.1	.4	3.0	.5	2.5
28 days	4.8	2.3	1.3	.3	1.6	.2	3.0	.5	3.0	.5	3.3	.5	3.2	.5	2.8
2 months	5.0	2.4	1.6	.3	2.0	.2	3.4	.6	3.4	.6	3.7	.7	3.6	.7	3.1
3 months	5.1	------	2.0	------	2.3	------	3.6	------	3.7	------	3.9	------	3.8	------	3.3
6 months	5.2	------	2.3	------	2.6	------	3.8	------	3.9	------	4.1	------	4.1	------	3.4
9 months	5.2	2.7	2.4	.6	2.8	.5	3.9	1.3	3.9	1.1	4.1	1.3	4.1	1.4	3.5
1 year	5.2	------	2.5	------	2.9	------	3.9	------	3.9	------	4.1	------	4.1	------	3.6

Time	Asphalt emulsions—Continued					Bituminous solutions									
	Material No.														
	[1]13	41	[1]41	42	[1]42	16	[1]16	18	[1]18	21	[1]21	23	[1]23	29	[1]29
¼ hour	0.0	0.0	0.0	0.3	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1 hour	0	0	0	.4	.2	0	0	0	0	0	0	0	0	0	.1
2 hours	0	0	0	.5	.2	0	0	0	0	0	0	0	0	0	.2
4 hours	0	0	0	.5	.3	0	0	0	.1	0	0	0	0	0	.2
24 hours	.1	.5	.1	.8	.4	0	0	.1	.5	.4	0	.1	0	.2	.8
48 hours	.1	1.4	.2	1.0	.5	0	0	.3	.7	.5	0	.1	0	.4	1.2
72 hours	.1	2.1	.3	1.1	.6	.1	0	.4	.9	.7	.1	.2	0	.6	1.5
7 days	.1	3.3	.4	1.4	.7	.2	0	.8	1.2	.7	.1	.2	0	.9	2.0
14 days	.1	4.1	.5	1.8	.8	.2	0	1.3	1.4	1.0	.1	.2	0	1.5	2.2
21 days	.2	4.3	.6	2.1	1.1	.3	.1	1.5	1.6	1.0	.1	.2	0	1.8	2.4
28 days	.2	4.5	.7	2.2	1.3	.4	.2	1.7	1.6	1.4	.1	.4	.1	2.4	2.6
2 months	.2	4.9	.8	2.4	1.6	.7	.2	2.0	1.6	1.7	.2	.4	.1	2.9	2.7
3 months	------	5.0	------	2.5	------	.8	------	2.2	------	1.7	------	.4	------	3.1	-----
6 months	------	5.0	------	2.6	------	.9	------	2.4	------	1.8	------	.4	------	3.3	-----
9 months	.5	5.0	1.4	2.7	2.2	1.1	.5	2.6	2.0	1.8	.4	.5	.4	3.4	3.0
1 year	------	5.0	------	2.8	------	1.2	------	2.7	------	2.0	------	.6	------	3.5	-----

[1] Per cent absorption after immersion in water for one year and then dried to constant weight in air of the laboratory.

TABLE 4.—*Per cent absorption 3 by 6 inch concrete cylinders coated with surface waterproofing materials*—Continued

Time	Bituminous solutions—Continued		Finely ground iron						Cement coatings					
	Material No.													
	31	[1] 31	17	[1] 17	27	[1] 27	43	[1] 43	47	[1] 47	48	[1] 48	49	[1] 49
¼ hour	0.0	0.0	0.7	0.4	1.4	0.2	0.5	0.2	0.8	0.0	0.5	0.1	0.4	0.1
1 hour	0	.1	1.5	.8	2.3	.2	.7	.4	2.0	0	.8	.2	.8	.2
2 hours	0	.1	2.1	.9	2.8	.4	1.1	.5	2.7	0	1.1	.2	1.1	.2
4 hours	.1	.1	2.6	1.3	3.4	.4	1.5	.7	3.5	0	1.3	.2	1.4	.4
24 hours	.3	.5	3.8	2.1	4.5	.7	3.5	1.3	4.3	0	2.4	.4	2.3	.6
48 hours	1.3	.8	3.9	2.5	4.6	.8	3.9	1.6	4.4	0	2.9	.4	2.8	.6
72 hours	1.8	1.2	3.9	2.7	4.7	.8	4.0	1.8	4.5	0	3.0	.6	3.0	.7
7 days	2.3	2.0	4.1	3.0	4.8	1.1	4.2	2.1	4.5	.1	3.3	.7	3.3	.7
14 days	2.8	2.4	4.2	3.0	4.8	1.3	4.3	2.2	4.6	.1	3.4	.8	3.5	.8
21 days	2.9	2.6	4.2	3.1	4.8	1.4	4.5	2.5	4.6	.3	3.6	.9	3.9	.9
28 days	3.3	2.6	4.3	3.1	5.0	1.5	4.5	2.5	4.8	.4	3.7	.9	3.9	.9
2 months	3.5	2.7	4.6	3.1	5.2	1.5	4.6	2.6	5.0	.4	3.8	.9	4.1	1.0
3 months	3.5	------	4.6	------	5.2	------	4.6	------	5.1	------	4.0	------	4.3	------
6 months	3.6	------	4.8	------	5.3	------	4.7	------	5.2	------	4.2	------	4.5	------
9 months	3.7	2.9	4.9	3.4	5.3	1.8	4.8	2.7	5.3	1.0	4.4	1.2	4.8	1.5
1 year	3.8	------	4.9	------	5.4	------	4.8	------	5.3	------	4.5	------	4.8	------

Time	Transparent coatings													
	Material No.													
	Std.	Std.[1]	1	[1] 1	2	[1] 2	3	[1] 3	4	[1] 4	11	[1] 11	46	[1] 46	25
¼ hour	1.7	0.1	0.1	0.0	0.3	0.2	0.2	0.1	0.5	0.1	0.0	0.1	0.3	0.1	0.3
1 hour	2.9	.2	.3	.1	.4	.2	.4	.2	.8	.1	0	.2	.7	.1	.5
2 hours	3.5	.2	.5	.1	.5	.2	.5	.2	1.2	.1	0	.2	1.0	.1	.7
4 hours	4.0	.3	.8	.1	.6	.2	.6	.2	1.5	.1	0	.2	1.4	.1	1.0
24 hours	4.4	.9	2.7	.2	1.0	.5	.9	.4	3.3	.1	.2	.4	2.9	.2	2.3
48 hours	4.4	1.1	3.5	.3	1.2	.5	1.2	.4	3.8	.2	.4	.4	3.6	.2	3.0
72 hours	4.7	1.3	4.1	.5	1.3	.5	1.5	.4	4.1	.3	.6	.5	3.9	.3	3.4
7 days	4.7	1.7	4.4	.8	1.8	.5	1.8	.5	4.3	.5	.9	.6	4.2	.4	3.8
14 days	4.7	2.0	4.4	1.2	2.3	.6	2.2	.7	4.3	.6	1.0	.8	4.2	.5	4.0
21 days	4.8	2.2	4.4	1.4	2.5	.7	2.3	.7	4.4	.8	1.1	.9	4.5	.7	4.2
28 days	4.8	2.3	4.4	1.6	2.5	.8	2.4	.8	4.6	.9	1.2	.9	4.5	.7	4.5
2 months	5.0	2.4	4.6	1.8	2.9	.8	2.9	.8	4.7	1.2	1.7	1.0	4.7	.9	4.6
3 months	5.1	------	4.7	------	3.1	------	3.2	------	4.8	------	2.0	------	4.8	------	4.7
6 months	5.2	------	4.9	------	3.2	------	3.4	------	5.0	------	2.6	------	4.9	------	4.8
9 months	5.2	2.7	5.0	2.7	3.3	1.2	3.4	1.1	5.0	2.1	3.3	2.3	4.9	1.6	4.8
1 year	5.2	------	5.1	------	3.3	------	3.4	------	5.0	------	3.8	------	4.9	------	4.8

[1] Per cent absorption after immersion in water for one year and then dried to constant weight in air of the laboratory.

TABLE 4.—*Per cent absorption 3 by 6 inch concrete cylinders coated with surface waterproofing materials*—Continued

Time	Transparent coatings—Continued														
	Material No.														
	[1] 25	37	[1] 37	12	[1] 12	15	[1] 15	24	[1] 24	26	[1] 26	28	[1] 28	32	[1] 32
¼ hour	0.0	0.0	0.1	0.5	0.1	0.2	0.0	1.2	0.1	0.7	0.1	0.3	0.0	0.5	0.0
1 hour	.1	.1	.1	1.4	.1	.6	.1	2.5	.2	1.7	.1	.8	0	1.3	.1
2 hours	.1	.1	.1	2.1	.1	.8	.1	3.2	.3	2.8	.2	1.4	.1	2.0	.1
4 hours	.2	.2	.2	3.0	.2	1.5	.1	4.0	.5	3.5	.2	2.3	.1	2.9	.1
24 hours	.3	.5	.2	3.5	.6	3.8	.3	4.4	1.2	4.5	.7	4.5	.4	4.1	.4
48 hours	.3	.8	.3	3.9	.9	4.4	.6	4.6	1.7	4.6	1.0	4.7	.6	4.2	.7
72 hours	.4	1.0	.3	4.1	1.0	4.6	.7	4.6	1.9	4.8	1.2	4.8	.8	4.2	.8
7 days	.5	1.5	.5	4.1	1.5	4.6	1.1	4.7	2.3	4.8	1.7	4.8	1.3	4.4	1.2
14 days	.5	1.7	.6	4.3	1.8	4.8	1.6	4.8	2.4	4.9	2.1	4.8	1.9	4.4	1.6
21 days	.7	1.9	.7	4.3	1.9	4.8	1.9	4.8	2.4	4.9	2.4	4.9	2.1	4.6	1.9
28 days	.7	1.9	.7	4.3	2.1	4.9	2.1	4.8	2.5	4.9	2.6	4.9	2.3	4.6	1.9
2 months	.9	2.2	.9	4.5	2.1	5.0	2.3	5.1	2.6	5.1	2.7	5.2	2.6	4.7	2.1
3 months	-----	2.3	-----	4.6	-----	5.1	-----	5.2	-----	5.1	-----	5.2	-----	4.7	-----
6 months	-----	2.6	-----	4.6	-----	5.1	-----	5.2	-----	5.2	-----	5.2	-----	4.9	-----
9 months	1.2	2.7	1.3	4.6	2.3	5.2	2.9	5.2	2.7	5.2	2.8	5.2	3.0	4.9	2.5
1 year	-----	2.8	-----	4.6	-----	5.2	-----	5.2	-----	5.2	-----	5.2	-----	4.9	-----

Time	Transparent coatings—Continued														
	Material No.														
	35	[1] 35	38	[1] 38	39	[1] 39	40	[1] 40	36	[1] 36	19	[1] 19	50	[1] 50	
¼ hour	0.3	0.0	0.2	0.0	0.2	0.1	0.2	0.1	0.3	0.1	0.4	0.0	0.5	0.1	
1 hour	.5	0	.4	.1	.5	.1	.6	.1	.6	.1	1.0	.1	1.5	.2	
2 hours	.9	0	.7	.2	.7	.2	1.1	.1	1.0	.1	1.8	.1	2.5	.2	
4 hours	1.5	0	1.3	.2	1.2	.2	1.5	.1	1.6	.2	2.8	.2	3.3	.4	
24 hours	3.8	.2	2.8	.6	2.9	.6	3.6	.5	3.7	.4	4.5	.6	4.1	.9	
48 hours	4.6	.4	3.7	.9	3.7	.8	4.3	.7	4.4	.6	4.5	.8	4.2	1.2	
72 hours	4.7	.5	3.9	1.1	3.8	1.0	4.3	.8	4.4	.8	4.7	1.0	4.2	1.4	
7 days	4.9	.9	4.5	1.7	4.2	1.5	4.5	1.2	4.4	1.2	4.7	1.5	4.3	1.7	
14 days	4.9	1.3	4.6	2.0	4.3	1.6	4.6	1.7	4.4	1.7	4.9	1.9	4.4	2.1	
21 days	4.9	1.6	4.8	2.1	4.5	2.1	4.7	1.9	4.6	2.0	5.0	2.3	4.8	2.2	
28 days	4.9	1.8	4.8	2.1	4.5	2.1	4.7	1.9	4.6	2.2	5.0	2.4	4.8	2.3	
2 months	5.2	2.3	5.0	2.3	4.9	2.3	5.0	2.1	4.8	2.5	5.1	2.6	4.9	2.3	
3 months	5.2	-----	5.1	-----	5.0	-----	5.1	-----	4.9	-----	5.2	-----	5.0	-----	
6 months	5.3	-----	5.1	-----	5.1	-----	5.1	-----	5.0	-----	5.4	-----	5.1	-----	
9 months	5.3	2.8	5.2	2.5	5.1	2.5	5.3	2.5	5.0	2.9	5.4	3.0	5.1	2.5	
1 year	5.3	-----	5.2	-----	5.1	-----	5.3	-----	5.0	-----	5.4	-----	5.1	-----	

Time	Paints and varnishes														
	Material No.														
	14	[1] 14	20	[1] 20	22	[1] 22	30	[1] 30	33 and 34	[1] 33 and 34	44	[1] 44	45	[1] 45	
¼ hour	0.1	0.1	0.5	0.0	0.0	0.1	0.0	0.1	0.0	0.1	0.0	0.0	0.0	0.1	
1 hour	.1	.2	1.0	.1	0	.2	0	.2	0	.2	0	.1	0	.1	
2 hours	.1	.2	1.6	.1	0	.2	0	.3	0	.5	0	.1	0	.1	
4 hours	.1	.3	2.4	.2	0	.2	0	.4	0	.7	.1	.2	0	.2	
24 hours	.4	.5	4.0	.5	.2	.4	.1	1.0	.1	1.6	.3	.3	0	.7	
48 hours	.6	.7	4.2	.6	.2	.5	.3	1.3	.3	2.1	.3	.4	.1	1.1	
72 hours	.6	.9	4.3	.8	.3	.6	.4	1.5	.3	2.3	.4	.4	.3	1.4	
7 days	.9	1.1	4.3	1.1	.5	.9	.5	2.1	.4	2.6	.6	.6	1.0	2.2	
14 days	1.2	1.5	4.4	1.4	.8	1.3	.8	2.4	.5	3.2	.9	.8	2.1	2.8	
21 days	1.5	1.7	4.5	1.6	1.1	1.5	1.2	2.5	.6	3.3	1.2	.9	2.8	3.0	
28 days	1.6	1.7	4.5	1.8	1.3	1.6	1.4	2.6	.7	3.4	1.4	.9	3.3	3.0	
2 months	2.1	2.1	4.8	1.8	2.1	1.9	3.0	2.8	1.2	3.5	2.0	1.1	3.8	3.1	
3 months	2.5	-----	4.8	-----	2.7	-----	4.3	-----	2.6	-----	2.5	-----	4.2	-----	
6 months	3.4	-----	4.9	-----	3.6	-----	4.8	-----	4.6	-----	3.1	-----	4.3	-----	
9 months	4.4	2.9	4.9	2.3	4.2	2.6	4.8	3.0	5.0	3.7	3.3	1.9	4.3	3.3	
1 year	5.2	-----	4.9	-----	4.4	-----	4.9	-----	5.1	-----	3.5	-----	4.4	-----	

[1] Per cent absorption after immersion in water for one year and then dried to constant weight in air of the laboratory.

XI. SUMMARY (SURFACE)

1. All of the surface coated concrete included in this investigation were less absorbent than the uncoated concrete for the first few periods (four hours) of immersion in water.

2. The most efficient coatings were some of the asphalt emulsions and bituminous solutions.

3. Linseed oil, China wood oil, and varnish were the most efficient transparent coatings.

4. Paints were quite effective for the first few months, but eventually broke down.

5. Drying out of the specimens after having been immersed in water for a year generally materially reduced the absorption of both the coated and uncoated specimens.

6. If the amount by which the absorption of the uncoated specimen has been reduced by drying, is deducted from the absorption of the coated specimen after immersion for nine months, it will be noted that the resulting figure is very generally lower than the absorption at nine months of the coated specimen after drying. Therefore, the apparent reduction in the absorption of the coated specimen resulting from drying is due to the lower absorption of the concrete and not to any change in character of the coating.

XII. RÉSUMÉ AND CONCLUSIONS

1. This investigation, like that carried out previously by this bureau and reported in its Technologic Paper No. 3 shows the difficulty of demonstrating in the laboratory the value of waterproofings, both integral and for surfacing. It is not a difficult matter to make a concrete that is impermeable to water under heads as great as 20 lbs./in.^{2} Such pressures exceed those encountered in by far the greater majority of concrete structures. Hence, since concrete can be so made without the use of waterpoofings, they would seem to be needless.

2. But in the placing of even very excellent concrete, it happens that it may become segregated partially into its constituents in certain places. When such places are too lean in mortar or cement paste, they will permit of the passage of water and consequently waterproofings are a matter of consideration. Doubtlessly some of the integral agents do give an unctuousness and ease of placing which tends to prevent segregation. Also others are of a nature such as to render concrete water repellent when sprinkled or subject to the precipitation of rain. Further, some might react with the cement so as to reduce voids in segregated portions through an unusual swelling of the hydrated cement. Hence, it does seem that these materials should be subject of study.

3. The lean concrete used was purposely adopted as simulating the lean segregated portion of concrete through which leakage generally occurs. If the integral waterproofings could reduce its permeability, they should be considered as of some merit. Some have been found to be of this nature; others seem to be valueless.

4. The lapse of time since the bureau's first study of such materials has not been prolific in producing new waterproofing agents. The names of the products are generally different, but a study of their

composition shows that they are, with few exceptions, of the same nature as previously. The ammonical copper solution of cellulose seems to be the only distinctly different new material.

5. The autogenous sealing up of the slightly leaking concrete seems to be quite an effective means of obtaining water tightness. This condition seems to result just as readily when no waterproofing agent is present as when one is.

6. The marked increase in permeability on drying the concrete specimens also characterizes field concrete. Although not carried out in this study, repeated wetting and drying generally gradually reduces leakage, however, only provided the leakage originally is not too great. In such a case, solution of the concrete results in increased permeability.

7. Attention needs hardly to be called to the fact that integral compounds are valueless if the concrete cracks through settlement, shrinkage, etc.

8. The simpler materials, such as the stearates, which can be bought in open competitive markets without paying for fanciful trade names are as effective as any.

9. Calcium chloride, although it can be readily purchased as such, is still a marked favorite, at least with sellers, under striking names and further camouflaged through the use of dyes.

10. The water emulsions of asphalt are relatively new, and generally their efficiency is well demonstrated by this study. It would seem, however, that manufacturers of these products should give them further study particularly as to the mineral extenders which they are incorporating in them. Although the data are meager, it appears that asbestos is a better mineral extender than clay. The cut asphalt applied as paints also gave good results. It should be remembered, however, that a year is a short period in the required life of a coating in actual service.

11. The coatings composed largely of inorganic pastes, such as iron oxide, cement, etc., gave poor results according to the test procedure used. Such coatings still have enough finer pores to permit of sufficient capillarity to give a high absorption. It is possible that under a higher head they might appear more promising. The paint coatings act also rather poorly apparently for the same reason.

12. Some of the transparent coatings gave good results. Striking among these are such readily obtainable materials as linseed and China wood (tung) oil.

13. In the case of leakage due to cracks following settlement or shrinkage, the use of coatings tending to seal over autogeneously should be considered in preference to the others not having this property. Such consideraion would bring the bituminous coatings to the fore.

XIII. ACKNOWLEDGMENTS

The author wishes to express his appreciation of the aid and cooperation of the following: W. Dean Kimmel in the preparation and testing of the specimens used in the investigation; to W. H. Cannon for the chemical analyses of the materials used; and to G. L. Kalousek for the compilation and preparation of data.

WASHINGTON, October 23, 1931.

THE EFFECT OF pH ON THE PHOTOCHEMICAL DECOMPOSITION OF SILK

By Milton Harris and Daniel A. Jessup

ABSTRACT

The extent to which silk is weakened by light depends upon its "pH" (as defined by its extract), other factors remaining constant. The maximum stability is found at about pH 10. Above pH 11 and below pH 3 the stability decreases rapidly. In the neutral region, pH 6 to pH 8, silk is less resistant to light than when it is more acid or alkaline. Silk treated with tenth normal sodium hydroxide solution is more stable to the action of light than either the untreated silk or silk treated with tenth normal sulphuric-acid solution. The acid-treated silk is least stable. These facts have an important bearing on practical silk finishing as well as on the nature of the action of light on silk.

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I. INTRODUCTION

Although silk is one of the strongest fibers known, its susceptibility to attack by light has been the source of considerable trouble, especially where the fabric has been exposed for any length of time. Formerly many investigators believed that only silk containing metallic weighting was attacked by light, but recent work has shown that the purest silk is affected.

Concerning the nature and mechanism of the breakdown, there are many and diversified opinions substantiated by little experimental work. Doree [1] states that the breakdown is caused by ultra-violet rays, acting either alone or in conjunction with the ozone produced by them. K. Homolka [2] and P. M. Grempe [3] state that the weakening of silk fibers by radiation is caused by the short ultra-violet rays from the sun. However, it should be noted that the sun's rays do not contain much short wave length ultra-violet and that this radiation does not pass through ordinary glass. (Radiation which passes through ordinary glass weakens silk.)

Herman [4] studied the effect of radiation on silk, using the mercury arc lamp. His results indicate that the radiation acts directly on the silk and that the deterioration is not a secondary reaction due to the ozone produced by the radiation.

[1] Doree, Charles and Dyer, Joseph W. W., Some Effects of the Action of Ultra-Violet Light on Cotton Fabrics, J. Soc. Dyers and Colourists, vol. 33, pp. 17–19; January, 1917.
[2] Homolka, Karl, Behandlung der Seide um ihre Widerstandskraft gegen die Einwirkung des Lichtes zur erholen, Melliand's Textilber. vol 5, p. 584; 1925.
[3] Grempe, P. Max, Bewahrung von Kunstseide und Seide bei Sonnenlicht und Wetter, Kunstseide vol. 9, pp. 462–463; 1927.
[4] Hermann, P., Ueber die Einwirkung der ultravioletten Strahlen auf Farb und Faserstoffsysteme, Melliand's Textilber. vol. 5, pp. 745–749; 1924.

While the experimental worker in textile fields has limited his studies largely to the effect of light exposure on tensile strength, the protein chemist has studied the chemical changes produced by light. Schanz [5] has shown that heat and light effect chemical changes in egg and serum proteins in acid and alkaline solutions and that the action is increased by the presence of oxygen. By exposure to sunlight, Effront [6] decomposed amino acids and protein matter in alkaline solution with the formation of ammonia and volatile acids. He found that sterile solutions of peptones exposed to sunlight decompose with formation of peroxide, nitrates, ammonia, and volatile acids. He concluded that the active agent was hydrogen peroxide, as this substance is known to decompose peptones and amino acids.

II. EXPERIMENTAL METHODS

A suitable and reproducible accelerated aging test was obtained by exposure to the light of a glass inclosed carbon arc, the external physical conditions being held constant. This was accomplished by placing the samples in a cabinet (15 by 15 by 15 inches) having a window of a special glass which is more transparent than window glass to the shorter wave lengths. The total radiation at a distance of 15 inches from the center, at right angles to the arc, operated on a current of 12.6 amperes, is 0.075 watts per cm^2. The temperature of the box was kept at 70° C. by a small fan for circulation and a thermostat control, most of the heat being supplied by radiation from the arc and the remaining heat from a carbon filament lamp bulb. A relative humidity of about 75 per cent was maintained by a saturated solution of sodium chloride.

Tests were made on pure silk which had been carefully boiled off and kept in the dark. Warpwise strips 48 inches long and about 1¼ inches wide were cut into 6-inch lengths. Enough warp threads were then removed to make each strip 1 inch wide. Each sample was allowed to remain in a solution of known pH for 10 minutes after which the excess liquor was removed by centrifuging for three minutes and subsequent drying in the dark.

The pH of the solutions was determined with the quinhydrone and hydrogen electrodes. The "pH" of the cloth (as defined by its extract) before and after exposure was obtained by extracting a standard sample for one hour with 50 cc of water, using an Underwriter extraction cup. The pH of the resulting solution was taken to be that of the cloth.

The tensile strength of the samples was measured on a pendulum type of testing machine. All samples were thoroughly conditioned and tested in a room maintained at a relative humidity of 65 per cent and a temperature of 70° F. The average strength of three to five samples is reported.

[5] Schanz, Fritz, Die Lichtreaktion der Eiweisskörper Arch. ges. Physiol., vol. 164, pp. 445–456; 1916.
[6] Effront, Jean, Action de la lumière et de l'eau oxygénée sur les matieres albuminoïdes et acides amidés, Compt. rend, vol. 154, pp. 1111–1114; 1912.

III. EXPERIMENTAL RESULTS

In order to determine the relative effects of the chemical treatment, light, and heat, three sets of samples were prepared. Each set was treated with solutions of sodium hydroxide or sulphuric acid ranging in pH from 1 to 13. The first set was allowed to stand in the dark at room temperature, the second set was exposed to a temperature of 70° C., and a relative humidity of 75 per cent without light, and the third set was treated as the second except that it was exposed to the light of the carbon arc. All exposures were for 30 hours. The breaking strengths of the samples are gi ven in Table 1.

TABLE 1.—*Relative effects of pH, heat and light on the breaking strength of silk cloth*

pH (±0.1)	In dark, room temperature	Breaking strength in dark, 70° C. and 75 per cent R. H.	Exposed to carbon arc radiation, 70° C. and 75 per cent R. H.
	Lbs. per in.	*Lbs. per in.*	*Lbs. per in.*
1	35	19	5
3	50	51	40
5	48	52	41
7	51	51	40
9	55	50	44
10	49	46	46
13	52	36	32

It is apparent from the results that in all cases, with the exception of pH 10 the breakdown obtained was accelerated by the action of the light. However, it is known that proteins in general are very susceptible to acid or alkali concentrations of 0.1 normal or greater. Even under these extreme conditions, the tendering was increased by exposure to the light.

Three sets of samples were prepared and treated so that the pH of the cloth ranged from 1 to 13. These were all given a 30-hour exposure and the average strength at each pH was taken. The following results were obtained:

TABLE 2.—*Effect of light on the breaking strength of silk cloth* [1] *at varying pH values*

pH (±0.1)	Breaking strength	pH (±0.1)	Breaking strength
	Lbs. per inch		*Lbs. per inch*
1	0	7	75
2	38	8	81
3	72	9	86
4	77	10	96
5	81	11	89
6	78	13	22

[1] Silk used here was of a heavier quality than that used in Table 1.

Several interesting points are portrayed here. As is evident from Figure 1, there is a definite region of maximum stability at about pH 10. The strength falls off rapidly below pH 3 and above pH 11. In the intervening range, there appears to be a minimum in the neutral region. Assuming that the protein material unites with small amounts of acid or alkali to form protein salts, the evidence indicates that the salts thus formed are more stable toward photochemical decomposition than the pure protein. Protein salts are probably also formed above pH 11 and below pH 3, but in these cases excessive

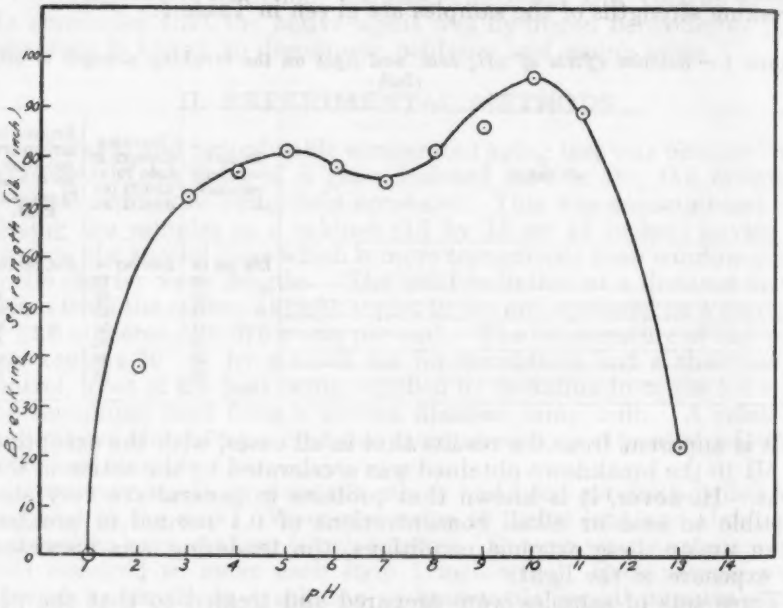

FIGURE 1.—*Effect of light on the breaking strength of silk cloth at varying pH values*

deterioration is more than likely caused by direct action of the excess acid and alkali.

An analogous reaction takes place in the photochemical oxidation of adrenaline. Vacek [7] found that light accelerates the reaction considerably. He observed that aqueous solutions of adrenaline decompose much more rapidly than solutions of adrenaline in dilute hydrochloric acid in which adrenaline hydrochloride is formed. Preliminary experimental work indicates that the decomposition of silk by light is a photooxidation reaction.

The relative rates of deterioration were determined by the following scheme: The first set of samples was treated with a solution of 0.1 *N* sodium hydroxide, the second with a solution of 0.1 *N* sulphuric acid, and the third was untreated.

[7] Vacek, Tomas, Oxidation of Adrenaline, Biochem. J., vol. 21, p. 457; 1927.

TABLE 3.—*Effect of light on the breaking strength of silk cloth treated with 0.1 N NaOH and with 0.1 N H_2SO_4*

Time (hours of exposure)	Breaking strength (pounds per inch)		
	No treatment	0.1 *N* NaOH	0.1 *N* H_2SO_4
0	98		
5		99	80
15		98	63
20		95	53
25		102	45
30	82	88	38
50		75	22
75	50	59	
100		56	
130	21	48	

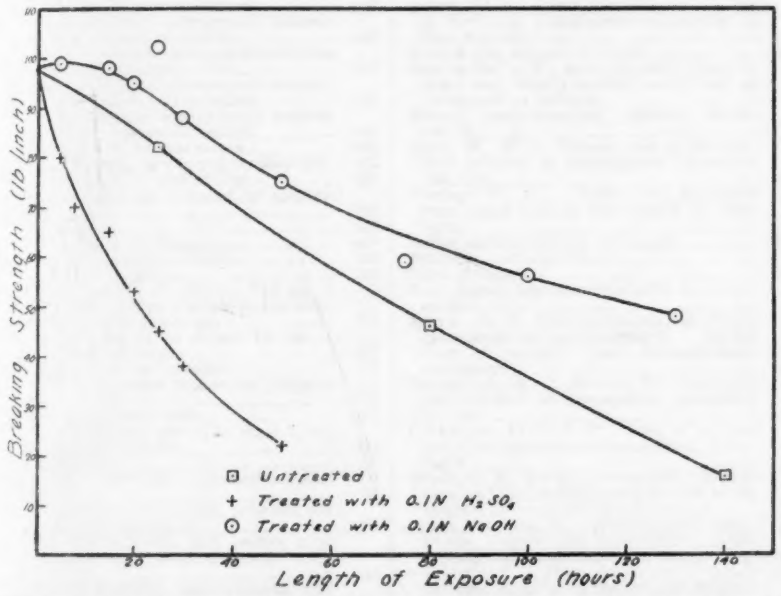

FIGURE 2.—*Effect of light on the breaking strength of silk cloth treated with 0.1 N NaOH and with 0.1 N H_2SO_4*

The results in Table 3 and also in Figure 2 show the relative stability of neutral, acid, and alkali treated silk to light. After a 50-hour exposure the acid-treated sample had lost 67 per cent of its original strength while the alkali-treated sample had lost only 23 per cent.

IV. CONCLUSION AND PRACTICAL SIGNIFICANCE

These experiments show that silk decreases in strength on exposure to light and that the rate of deterioration depends upon the pH to which the silk has been finished. Contrary to what might be expected from the fact that alkalies hydrolyze proteins more rapidly than do acids, silk treated with 0.1 *N* NaOH is more stable in light

than silk treated with 0.1 N H_2SO_4. Silk whose water extract has a pH of about 10 shows maximum stability to light.

The stability decreases rapidly above pH 11 and below pH 3. From pH 6 to pH 8; that is, in the region of neutrality, silk is less resistant to light than when it is more acid or alkaline.

These observations lead at once to the very practical conclusion that commercial finishing should leave silk at a "pH" of about 10 if the maximum stability to light is desired. Whether other considerations will permit of such finishing must be decided for the materials to be processed.

WASHINGTON, October 9, 1931.

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